Modeling of industrial NH₃ oxidation on Pt catalysts: The effect of local mass transfer on N₂O selectivity



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Zusammenfassung

Zahlreiche Anstrengungen sind unternommen worden, um den Mechanismus der heterogen-katalysierten Ammoniakoxidation auf molekularer Ebene aufzuklären. Dennoch finden sich nur wenige Arbeiten, die das Verhalten etablierter Reaktionsmechanismen unter industriellen Bedingungen und Massentransferlimitierung untersuchen. In dieser Arbeit wird die industrielle NH₃-Oxidation an Pt-Netzkatalysatoren mit Hilfe der Modellierung reaktiver Strömungen untersucht. Dazu werden Simulationen durchgeführt, in denen eine mechanistische Beschreibung der Oberflächenchemie mit der Berechnung von Strömungs-, Temperatur- und Konzentrationsfeldern um die Platin-Katalysatordrähte gekoppelt ist.

Die von den Modellen vorhergesagte integrale N₂O-Selektivität, sowie Temperatur- und Konzentrationsfelder, stimmen mit den (limitiert verfügbaren) experimentellen Daten und den in der industriellen Praxis gemachten Beobachtungen überein. Dabei zeigt sich, dass die axialen Temperaturgradienten von der Lewis-Zahl des Reaktionsgases und dem Betriebsdruck abhängen. Die Simulationen bestätigen den im Experiment beobachteten Abfall der integralen N₂O Selektivität mit abnehmender Strömungsgeschwindigkeit, zunehmenden Drahtdurchmesser und Draht-zu-Draht Abstand sowie vergrößerter Oberfläche auf Grund der topologischen Restrukturierung des Katalysators. Im Besonderen zeigen die Berechnungen, dass das Zusammenspiel von lokalem Strömungsfeld und Oberflächenchemie zu einer Variation in den Selektivitäten der Nebenprodukte N2O und N2 auf dem Katalysatornetz führt: Im Vergleich zur Rückseite eines umströmten Drahtes, wird auf der Vorderseite eine erhöhte Selektivität zu den Nebenprodukten beobachtet. Befindet sich ein Draht im Strömungsschatten eines davorliegenden Drahtes, so weist dieser eine verringerte Selektivität auf. An den Staupunkten tiefer liegender Drähte, auf welche die Strömung auf Grund des Kanalisierungseffektes der sich stromaufwärts befindlichen Drähte mit einer erhöhten Geschwindigkeit auftrifft, zeigt sich wiederum eine erhöhte Nebenprodukt-Selektivität. All diese Ergebnisse zeigen, wie die Intensität des Massentransfers und die Selektivität an einem bestimmten Draht durch die Positionierung der umliegenden Drähte und deren Einfluss auf das lokale Strömungsfeld beinflusst werden.

Das Konzept der *degree of mass transfer control* beschreibt die Sensitivität der Produkt-Selektivitäten auf Änderungen der Massentransfersintensität. Aus Strömungssimulationen der Katalysatorstrukturen können Informationen über die Verteilung von lokalen Massentransferkoeffizienten über den Katalysator erhalten werden. Die Kombination der degree of mass transfer control mit den Strömungssimulationen stellt ein neues und universelles Instrument zur Untersuchung und Entwicklung von Katalysatoren für Massentransfer-limitierte chemische Prozesse dar. Das Potential dieser Methodik wird anhand der industriellen Ammoniakoxidation für Netz-Katalysatoren verschiedener geometrischer Komplexität aufgezeigt. Dieses kombinierte Konzept kann auch auf der Mikroskala des Katalysators angewendet werden, wie am Beispiel eines Pt-Drahtes mit restrukturierter Oberfläche demonstriert wird.

Durch Kombination von Large Eddy Simulationen mit detaillierter Oberflächenchemie wird der Einfluss von turbulenter Strömung auf das katalytische Verhalten eines Pt-Einzeldrahtes sowie einer Konfiguration mehrerer paralleler Drahtreihen untersucht. Obwohl ausgeprägte Fluktuationen der lokalen Sherwood-Zahl und damit einhergehend der N₂O-Selektivität beobachtet wird, unterscheidet sich die resultierende integrale N₂O-Selektivität nur geringfügig von der, welche im Fall einer laminaren Strömung erhalten wird.

Abstract

Despite the enormous effort spent on the investigation of heterogeneously catalized ammonia oxidation at the molecular scale, there is surprisingly little work that studies the behavior of established reaction mechanisms under industrial conditions with mass transfer limitations being present. In this work, the industrial ammonia oxidation on platinum catalyst gauzes is investigated by means of reactive flow simulations. To this end, a mechanistic description of the surface chemistry is coupled with the computation of flow-, temperature- and concentration fields around the Pt wires.

The simulations predict integral N_2O selectivities, as well as temperature and concentration fields in line with the industrial experience and (limited available) experimental data. It is demonstrated that the axial temperature gradient inside the gauze is controlled by the Lewis number of the reacting gas and the operating pressure. The experimentally observed decrease in integral N_2O selectivity with decreasing flow velocity, increasing wire diameter, increasing wire-to-wire distance, as well as increased surface area, due to catalyst surface reconstruction, is reproduced by the models. In particular it is found that the local interaction of flow-field and surface chemistry leads to a variation in the local selectivity towards the by-products N_2O and N_2 across the gauze: The selectivity of side products is higher on the front side of the wire than on the rear side. A reduced selectivity is observed, where one wire is shadowed by another. At the stagnation points, where upstream wires direct the flow so that it hits a downstream wire with higher velocity, an increased side product selectivity is observed. These examples show that, through the flow-directing effect of upstream wires, the mass transfer intensity and thus the selectivity on an individual wire is influenced by the presence of other wires.

The *degree of mass transfer control*, i.e. the sensitivity of product selectivity with respect to changes in mass transfer intensity, provides a mathematical formalism allowing to quantify the flow-induced effect of local mass transfer on the product selectivity. Combined with flow simulations of catalyst structures, yielding the distribution of local mass transfer coefficients throughout the catalyst, this type of sensitivity analysis constitutes a novel and universal instrument to investigate and design structured catalysts for chemical reactions being controlled by external mass transfer. With the industrial ammonia oxidation as a test case, the capabilities of this tool are demonstrated for gauze catalysts with different levels of geometric complexity. This concept also finds applications at the catalyst microscale, which is demonstrated using a Pt wire with a restructured surface as an example.

Finally, the influence of upstream turbulence on the catalytic performance of a single Pt cylinder as well as a stack of multiple wires is studied, combining large eddy simulations with detailed surface chemistry. Although significant time-dependent fluctuations in the local Sherwood number and N_2O selectivity can be observed along the wires, in both cases the integral N_2O selectivity only slightly deviates from the results found in case of laminar flow.

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Nomenclature

Latin symbols

Symbol	Description	Unit
a	Absorption coefficient	_
$a_{\rm s}$	Surface-to-volume ratio	m^{-1}
A	Area	m^2
A	System of algebraic equations	_
b	Temperature exponent	_
c	Concentration	$mol m^{-3}$
c_{b}	Bulk concentration	$mol m^{-3}$
c_{film}	Film concentration	$mol m^{-3}$
$c_{\rm s}$	Near-surface concentration	$mol m^{-3}$
c_p	Specific heat capacity at constant pressure	$ m J~kg^{-1}~K^{-1}$
$c_{p,m}$	Molar heat capacity at constant pressure	$\mathrm{J}~\mathrm{mol}^{-1}~\mathrm{K}^{-1}$
$c_{v,m}$	Molar heat capacity at constant volume	$\mathrm{J}~\mathrm{mol}^{-1}~\mathrm{K}^{-1}$
D	System of differential equations	_
D	Diffusion coefficient	$m^{-2} s^{-1}$
D	Wire distance	m
D_m	Mixture averaged diffusion coefficient	$m^2 s^{-1}$
$d_{ m w}$	Wire diameter	m
$E_{\rm a}$	Activation energy	$ m J~mol^{-1}$
F_{Γ}	Surface enlargement factor	_
f_v	Volumetric force	$kg m^{-2} s^{-1}$
f	Frequency	s^{-1}
$f_{ m d}$	Fraction of diffusively reflected radiation	_
$\Delta_{ m R} G^0$	Standard state Gibbs energy of reaction	$ m J~mol^{-1}$
h	Perturbation factor	_
h	Specific enthalpy	$ m J~kg^{-1}$
H	Molar enthalpy	J mol ⁻¹
$\Delta_{\rm f} H^0$	Standard-state enthalpy of formation	$ m J~mol^{-1}$
$\Delta_{ m R} H^0$	Standard-state enthalpy of reaction	$ m J~mol^{-1}$
$\Delta_{\rm R} H^{\Rightarrow}$	Standard-state enthalpy of reaction at 298.15 K	$ m J~mol^{-1}$
Ι	Identity matrix	_
I_{rad}	Radiant intensity	$\mathrm{W}~\mathrm{m}^{-2}~\mathrm{sr}^{-1}$
J	Molar flux	$mol m^{-2} s^{-1}$
J^m	Mass flux	${\rm kg}~{\rm m}^{-2}~{\rm s}^{-1}$
k	Rate coefficient	a.u.
k_0	Pre-exponential factor	a.u.

Symbol	Description	Unit
$k_{ m t}$	Turbulence kinetic energy	$m^2 s^{-2}$
Kn	Knudsen number	_
L	Characteristic length	m
Le	Lewis umber	_
m	Mass	kg
M	Molar mass	$kg mol^{-1}$
\overline{M}	Mean molar mass	$kg mol^{-1}$
Ma	Mach number	_
\boldsymbol{n}	Normal vector	_
n	Refractive index	_
n	Reaction order	_
n_S	Selectivity order	_
\tilde{Nu}	Nusselt number	_
p	Pressure	Pa
Pr	Prandtl number	_
ġ	Heat flux	$\mathrm{W}~\mathrm{m}^{-2}$
r	Rate of elementary reaction	s^{-1}
r	Position vector	m
R	Surface reaction rate	$mol m^{-2} s^{-1}$
Re	Revnolds number	_
s	Direction vector	_
$\frac{S}{S}$	Differential selectivity	_
$\widetilde{S}^{\mathrm{I}}$	Integral selectivity	_
\tilde{S}	Sticking coefficient	_
$\tilde{\Delta}_{\epsilon}S^0$	Standard-state entropy of formation	$J \text{mol}^{-1} \text{K}^{-1}$
$\Delta_{\rm D}S^0$	Standard-state entropy of reaction	$I \mod^{-1} K^{-1}$
$\frac{\Delta_{\rm R}}{S_{\rm C}}$	Normalized sensitivity of selectivity	_
S S	Mass source term	$kg m^{-3} s^{-1}$
S.	Heat source term	$W m^{-3}$
S_{h}	Normalized sensitivity coefficient	vv III
SC Sc	Schmidt number	_
SC Sh	Schinict humber	—
511 +	Time	_
ι	Tomporature	S V
T	Wire temperature	K V
1 _s	Valacity	$K = c^{-1}$
u	Average velocity	$m s^{-1}$
u_m	Average velocity	
x	Mole fraction	—
$x_{ m b}$	Buik mole fraction	—
$x_{\rm film}$	Film mole fraction	_
x_{s}	Near-surface mole fraction	_
X	Conversion	_
$X_{\rm all}$	All parameter degree of rate control	_
$X_{ m RC}$	Degree of rate control	-
$X_{ m RC}^{\prime\prime\prime}$	Degree of rate control with mass transfer	

Symbol	Description	Unit
$X_{\rm SC}$	Degree of selectivity control	-
$X_{ m SC}^m$	Degree of selectivity control with mass transfer	-
k _B	Boltzmann constant	$1.381 \cdot 10^{-23} \mathrm{J} \mathrm{K}^{-1}$
N_A	Avogadro constant	$6.022 \cdot 10^{23} \text{ mol}^{-1}$
R	Universal gas constant	$8.314 \text{ J} \text{ mol}^{-1} \text{ K}^{-1}$
σ	Stefan-Boltzmann constant	$5.670 \cdot 10^{-8} \text{ W m}^{-2} \text{ K}^{-1}$

Throughout this work, vector and matrix quantities will be denoted in **bold font**. The small letters i and j are used as counters and x, y, z are often utilized as generic coordinates.

Greek symbols

Symbol	Description	Unit
α	Heat transfer coefficient	${ m W}~{ m m}^{-2}~{ m K}^{-1}$
eta	Mass transfer coefficient	${ m m~s^{-1}}$
δ_{ij}	Kronecker-Delta	_
γ	Open area fraction	_
Γ	Site density	$ m mol~m^{-2}$
ϵ	Emissivity	_
ϵ	Potential depth of Lennard-Jones potential	J
heta	Surface coverage	_
λ	Thermal conductivity	$\mathrm{W}~\mathrm{m}^{-1}~\mathrm{K}^{-1}$
$\lambda_{ m m}$	Mean free path	m
μ	Dynamic viscosity	Pa s
$\mu_{ m t}$	Turbulence viscosity	Pa s
ν	Stoichiometric coefficient	_
ho	Density	${ m kg}~{ m m}^{-3}$
σ	Collision diameter	m
$\sigma_{ m m}$	Mean molecular diameter	m
$\sigma_{ m s}$	Scattering coefficient	_
$ au_{ij}$	Stress tensor	$\mathrm{kg}~\mathrm{m}^{-1}~\mathrm{s}^{-2}$
Φ	Porosity	_
Φ	Phase function	_
ϕ	General scalar	a.u.
ω	Mass fraction	_
Ω	Full solid angle	sr
$\Omega^{(l,s)^*}$	Reduced collision integral	_

Abbreviations

Abbreviation	Meaning
BET	Brunauer-Emmet-Teller
CAD	Computer aided design
CFD	Computational fluid dynamics
CFL	Courant-Friedrich-Lewis
СТ	Computer tomography
CV	Control volume
DAE	Differential algebraic equation
DFT	Density functional theory
FDM	Finite difference method
FEM	Finite element method
FVM	Finite volume method
GHG	Greenhouse gas
LES	Large eddy simulation
LHHW	Langmuir-Hinshelwood-Hougen-Watson
NSCR	Non-selective catalytic reduction
NS	Navier-Stokes
ODE	Ordinary differential equation
PDE	Partial differential equation
PDS	Power density spectrum
RANS	Reynolds-averaged Navier-Stokes
RMSE	Root mean square error
SCR	Selective catalytic reduction
SST	Shear stress transport
SUNDIALS	SUite of Nonlinear and DIfferential/ALgebraic Equation Solvers
TEM	Transmission electron microscopy

1. Introduction

Under the focus of the proceeding climate change and the increase in mean global temperature, the governments of many countries have put to force measures to reduce greenhouse gas (GHG) emissions, above all the emission of CO₂. In 2021 for example, Germany has agreed on being free of net green house gas emissions by the year 2045 [1]. To reach the 1.5 degree Celsius goal established in the Paris agreement in 2015 [2], society and industry need to turn towards carbon dioxide free or neutral technologies and processes. As a cornerstone of progress and our modern life, the chemical industry sector is a large contributor to global GHG emissions. This contribution is not only due to direct emissions, i.e. emissions that are a direct result of chemical conversion processes yielding the desired products, but also due to the sector's high energy demand, since the energy conversion processes involved still operate mainly on fossil fuels. Furthermore, most of the goods manufactured by the chemical industry still heavily rely on non-renewable feedstock, such as oil, coal or gas. As a consequence, the choice of raw materials leads to postponed net emissions further downstream the exploitation chain. According to the International Energy Agency (IEA), the chemical industry is responsible for approximately 7% of the global total GHG emissions [3]. This is mainly due to its high energy demand which accounts to about 10% of the global total final energy consumption, which equals roughly 30% of the total energy demand in the industrial sector.

However, in recent years a lot of scientific and engineering effort has been directed towards finding alternative feed stocks, process routes and products with focus on renewable resources. Much focus lies hereby on the utilization of hydrogen produced from regenerative energies (for example for Fischer-Tropsch synthesis and CO_2 hydrogenation). Furthermore, many existing processes and plants can be optimized in order to reduce GHG emissions or even to avoid them completely. This illustrates that within the chemical sector, there is a large potential but also responsibility to develop a clean and more efficient industry, making a significant contribution to reach the overall global emission targets.

With an annual production of 146 million tons (2014), ammonia ranks second among the largest commodities within the whole chemical industry, just behind sulfuric acid [4]. Manufactured in the Haber-Bosch process, its production consumes about 1% of the total global energy supply [5] and thus states a significant source of CO_2 emissions. These are mainly due to the production of hydrogen, which is besides atmospheric nitrogen the second, more crucial feed component, still heavily relying on fossil fuels, mostly on steam reforming of natural gas [6]. About 10% of the total ammonia produced is used in the Ostwald process for the production of nitric acid, resulting in a production of 55 million tons of pure HNO₃ per year (2014) [7]. The main part of the nitric acid - about 80% - goes into the manufacturing of fertilizers, where it is mainly converted together with ammonia to yield ammonium nitrate. Together with the Haber-Bosch process, the production of nitric acid forms the backbone of our modern society's fertilizer production. About 85% of the total ammonia produced ends up in fertilizer products, most of it being urea [4].

Therefore, the demand of nitric acid and ammonia are closely coupled with the the development of world population and standard of living. It is assumed that by 2050 the world population will reach 9.7 billion [8], compared to 7.8 billion in 2020. In addition, the global average living standard is increasing as well, thus the demand for nitric acid is still growing and is predicted to do so in the coming decades.

The first step in the 3-stage Ostwald process involves the combustion of ammonia in air over a Pt/Rh catalyst gauzes to yield NO, followed by a secondary oxidation to NO₂ and finally its absorption in water. This first stage is the most crucial in the process, as undesired side reactions lead to the formation of N₂ and N₂O, determining the selectivity and efficiency of the overall process. With total ammonia conversion and HNO₃-yields reaching up to 98%, the process is already quite efficient. Nevertheless, due to environmental issues, the formation of side products has gained increasing attention. N₂O has a global warming potential a approximately 300 times larger than that of CO₂ and is also involved in ozone depleting processes in the stratosphere [9]. Although nitrogen has no direct negative impact on the environment, its formation from NH₃ constitutes an indirect negative effect, due to the energy and CO₂ intensive production of the latter in the Haber-Bosch process. Due to the large scale of the process, even small improvements in its efficiency can lead to significant energy and GHG emission savings.

Carried out at high temperatures (\approx 900 °C), ammonia oxidation is a classic example of a heat and mass transfer controlled reaction. The diffusion limitations in combination with harsh reaction conditions, i.e. high combustion temperatures, elevated pressures up to 16 bar, as well as corrosive and toxic substances, have so far prevented scientists and engineers from a deep and comprehensive understanding of the overall process. It has proven hard, to some extent even impossible, to isolate and deconvolute the influence of different selectivity-governing effects in a conventional experiment. However, this detailed insight is essential for the rational improvement and optimization of the process.

To this end, industrial ammonia oxidation is an interesting field for the application of numerical models and simulation approaches, as modeling can help to close knowledge gaps as well as support and guide experimental investigations in areas, where experiments can provide an answer only with great effort. Nowadays powerful hardware and sophisticated software allow for the simultaneous solution of mass-, momentum-, heat and species balance equations even for complex problems in the field of chemical reaction engineering. There lies great potential in these *in silico* investigations, as they allow to examine different physical or chemical phenomena decoupled from all other effects with relatively low effort and costs.

In order to investigate ammonia oxidation under industrial conditions, in following work gauze scale simulations of reactive flow will be performed by coupling the solution of flow-, concentration- and temperature fields with detailed mechanistic kinetics of surface chemistry. Model catalysts with different level of complexity will be investigated, to provide a more fundamental understanding of the interplay between gas flow, mass- and heat transfer and surface chemistry and how these effects impact the overall performance of the catalyst. The simulations are supported by sensitivity analysis of the chemical kinetic system explicitly incorporating mass transfer effects. Such knowledge can then be used to assist design choices regarding the catalyst as well as the process as such.

2. Motivation and frame of this work

Although the Ostwald process has been introduced already in the early 20th century, only marginal improvements in reactor and catalyst design, as well as operation practices have been made during the last century. This is mainly due to a lack of knowledge regarding the interplay and connection of the different physical and chemical phenomena at the stage of the ammonia combustion. Even today, the process is far from being well understood. There might be two explanations for this:

First, mass transfer limitations and harsh reaction conditions (high temperature and pressure, corrosive media) have prevented scientists from carrying out the required investigations, as the respective experiments were too complex or even impossible to be carried out.

The second argument involves the high efficiency of the process. With possible yields up to 98 %, plant operators as well as scientists were not too much under pressure to get more sophisticated insights into the process. Thus operating and design decisions, leading to minor improvements, were justified and based mostly on empirical knowledge and experience, including out-dated models and views.

This picture, however, seems to have changed during the recent years. Driven by the upcoming political and social awareness of GHG emissions, as well as more stringent governmental regulations, the environmental aspects of the Ostwald process have come more and more into focus. Motivated by the large scale of the process and the significant impact that N_2O emission savings and more efficient NH_3 conversion can have on the environment as well as on the process viability, substantial fundamental research has been directed towards the mechanistic understanding of the chemical reaction. In earlier days, global Langmuir-Hinshelwood-Hougen-Watson (LHHW)-type kinetics have been used to describe the surface chemistry, taking into account the mutual inhibition of the different reactants. Later, advancements in surface science techniques allowed researchers to gain detailed insight into the individual elementary steps involved in the overall reaction scheme. As a consequence, nowadays there seems to be consensus throughout the literature on the mechanism and the important individual steps. This has led to numerous publications of kinetic models for Pt-catalyzed ammonia oxidation. Recently increasing work has also been dedicated towards deriving kinetic models from *ab initio* methods, such as DFT calculations.

Despite the effort, current mechanistic and kinetic models have not been well validated under industrial conditions. The inevitable mass transfer limitations and the strong exothermicity have prevented researchers to directly measure rates at conditions relevant for industrial ammonia oxidation. Instead, kinetic models have been parametrized using experimental data obtained either under vacuum conditions or at much lower temperatures. Surprisingly, there is only little work present, where these kinetic mechanisms have been applied and investigated in reactor-scale simulations. This is even more unexpected, as in order to compare these models with the observations in industrial reactors, the strong mass transfer limitation has to be accounted for, which requires knowledge about the flow-, concentration- and temperature field around the catalyst wires.

The importance of diffusion limitations in industrial ammonia oxidation has been recognized many years ago and the process still serves as a textbook example for a mass transfer limited process [7].

Earlier works published used concepts such as mass transfer coefficients or number of transfer units in order to determine the equipment of Pt catalyst gauzes required in a reactor. Other work investigated mass transfer characteristics for different catalyst gauzes using dimensionless correlations. However, all this research was focused on the effect of mass transfer intensity on the overall ammonia conversion and has neglected investigating its effect on the N₂O and N₂ selectivity. At the same time, research on surface chemistry has to some extend ignored the fact, that the reaction is mass transfer controlled. Recent DFT studies for example completely ignored any mass transfer effects, validating their kinetic model using bulk gas concentrations [10, 11]. Furthermore, mass transfer is often neglected, when scientists apply tools like *degree of rate control* or related concepts to evaluate the sensitivity of kinetic parameters. This shows, that in the existing literature, the investigation of mass transfer effects and the discussion of surface chemistry have been insufficiently coupled. To the authors' knowledge, the only exception is the work of Warner and Haynes, who combined a description of heat- and mass transfer by transfer coefficients with a treatment of surface chemistry by a surface kinetic model [12, 13]. However, treating the mass transfer in the entire gauze by a single averaged mass transfer coefficient, as done in these studies, does not allow to study the effect of local flow and mass transport on surface chemistry and hence on product selectivity. Such information on a locally resolved level is important since for example industrial practice empirically finds improved NO selectivity for more complex shaped gauze structures, an observation still lacking an explanation by the reaction engineering community.

The work following is dedicated to investigate the effects and interaction of gas flow and mass transfer with surface chemistry for industrial ammonia oxidation by the use of numerical models. Therefore, gauze scale flow simulations are carried out in which the solution of flow-, concentration and temperature fields is coupled with surface chemistry described by detailed kinetic models. The focus lies on gaining an understanding of how the selectivity of unwanted side products is influenced by local mass transfer effects and thus gauze geometry. Furthermore the question is tackled, how the incorporation of external mass transfer effects into the chemical mechanism influences the results of conventional kinetic sensitivity analysis such as *degree of rate control*. This knowledge is of high value for the further development of catalysts and the optimization of the overall process. The presentation of the results is subdivided into three chapters:

In chapter 5 two-dimensional flow simulations combined with detailed surface kinetics are are presented, to provide a deeper understanding of the underlying processes controlling the product selectivities and efficiency of industrial ammonia oxidation. Different physical phenomena and parameters such as gas velocity, pressure, radiation losses and geometric features of the catalyst will be examined in detail. The focus lies on the interplay between the local flow field and the induced mass transport effects on local concentration distributions near the catalyst surface and the chemical kinetics. With the insights gained, a possible explanation is given for the improvement in product selectivity observed when utilizing new shape designs for catalyst gauzes.

Chapter 6 focuses on a closer insight and quantification of local mass transfer effects on the surface chemistry. The concept of *degree of mass transfer control* is introduced to quantify how the selectivity of the catalyst is controlled by changes in the local mass transfer intensity. This concept is then combined with three-dimensional flow simulations of Pt catalyst geometries yielding a powerful tool to make predictions about the effect of catalyst shape on product selectivity. The study includes investigations of more complex woven gauze structures, as well as simulations resolving the catalysts microscale using Computer Tomography (CT) images of a restructured gauze.

The final chapter 7 presents first investigations on the influence of turbulent flow on the catalyst

performance. Due to turbulent flow upstream of the catalyst, the mass transfer intensity in the top layer gauzes is not only influenced by the shape of the catalyst, but also perturbed by fluctuations of the surrounding velocity field. Large eddy simulations (LES) of simplified gauze models are carried out to elucidate if upstream turbulence affects the catalyst performance and if such effects have to be incorporated into future reactor simulations.

3. Theoretical background

3.1. Ostwald process

The production of nitric acid via the Ostwald process is among the largest and most important industrial processes in the field of basic chemicals. The annual world production totaled 55 million tons of pure HNO₃ in 2014, thus making nitric acid one of the largest chemical commodities [7]. Together with the production of ammonia in the Haber-Bosch process, it represents the basis for the modern, nitrogen-based fertilizer industry, into which about 80% of the worlds produced nitric acid flow [7]. The remaining 20% go into the production of intermediates for polymers like polyamides (adipic acid, caprolactam) and polyurethanes (dinitrotoluene) or are used as nitration reagent for explosives, dyes or pharmaceutical products. Since the days of its development by the german chemist Wilhelm Ostwald and first applications in the chemical industry at the beginning of the 20th century [14], the process itself has undergone only marginal changes with selected enhancements concerning the reactor geometry, the catalyst or operation conditions. The process is conducted in three consecutive steps:

First, in a highly exothermic reaction ammonia is converted with atmospheric oxygen to yield nitric acid according to the following reaction:

$$4 \operatorname{NH}_3 + 5 \operatorname{O}_2 \longrightarrow 4 \operatorname{NO} + 6 \operatorname{H}_2 \operatorname{O} \qquad \Delta_{\mathrm{R}} H^{\circ} = -904 \, \mathrm{kJ} \, \mathrm{mol}^{-1} \tag{R1}$$

In the second step, the gas mixture is cooled down. In a gas phase reaction nitric oxide and the excess oxygen, as well as supplied secondary oxygen form nitrogen dioxide, which can dimerize to dinitrogen tetroxide:

$$2 \operatorname{NO} + \operatorname{O}_2 \longrightarrow 2 \operatorname{NO}_2 \qquad \Delta_{\mathrm{R}} H^{\circ} = -114 \,\mathrm{kJ} \,\mathrm{mol}^{-1}$$
 (R2)

$$2 \operatorname{NO}_2 \rightleftharpoons \operatorname{N}_2 \operatorname{O}_4 \quad \Delta_{\mathrm{R}} H^{\circ} = -58 \,\mathrm{kJ} \,\mathrm{mol}^{-1}$$
 (R3)

The last step of the Ostwald process is the reactive absorption of nitrogen dioxide, and dinitrogen tetroxide respectively, in water. Due to many reactions occurring in the gas and liquid phase with many species being invloved, the adsorption is rather complex [7] and therefore only the main route for the formation of nitric acid is shown. This involves the reaction of nitrogen dioxide with water to nitric acid and nitric oxide:

$$3 \operatorname{NO}_2 + \operatorname{H}_2 O \longrightarrow 2 \operatorname{HNO}_3 + \operatorname{NO} \qquad \Delta_{\mathrm{R}} H^{\circ} = -138 \,\mathrm{kJ} \,\mathrm{mol}^{-1}$$
 (R4)

Due to Le Chatelier's principle, high pressures favor the absorption and the formation of aqueous nitric acid, but at the same time reduce the ammonia conversion as well as the selectivity towards NO at

the burner stage. This problem can be overcome by introducing a second, higher pressure stage after the NH_3 oxidation, resulting in an increased absorption efficiency while maintaining high NO yields. The overall reaction for the production of nitric acid can be summarized as follows:

ne overall reaction for the production of intrie acid can be summarized as follows.

$$NH_3 + 2O_2 \longrightarrow HNO_3 + H_2O \qquad \Delta_R H^{\circ} = -330 \text{ kJ mol}^{-1}$$
(R5)

Figure 3.1 shows a simplified process scheme. A more detailed description of the process as a whole and its history is given in [13, 15, 16].



Figure 3.1.: Simplified flow chart of the Ostwald process, adapted from [15].

3.2. Industrial ammonia oxidation

The oxidation of ammonia is the crucial step of the Ostwald process on which most of the research and engineering efforts has been concentrated in the last century. Ammonia is converted over a Pt/Rh gauze catalyst at short contact times (≈ 1 ms) and gauze temperatures of 800 – 950 °C. Once the reaction has been started by ignition at the beginning of a campaign, it proceeds autothermal without supply of external heat, due to the high exothermicity (see R1). The formation of N₂ and N₂O occur as undesired side reactions according to:

$$4 \operatorname{NH}_3 + 3 \operatorname{O}_2 \longrightarrow 2 \operatorname{N}_2 + 6 \operatorname{H}_2 \operatorname{O} \qquad \Delta_{\mathrm{R}} H^{\circ} = -1260 \text{ kJ mol}^{-1}$$
(R6)

$$2 \operatorname{NH}_3 + 2 \operatorname{O}_2 \longrightarrow \operatorname{N}_2 \operatorname{O} + 3 \operatorname{H}_2 \operatorname{O} \qquad \Delta_{\mathrm{R}} H^{\oplus} = -552 \text{ kJ mol}^{-1}$$
(R7)

Other unwanted side reactions are the reduction of NO with unconverted NH₃

$$4 \operatorname{NO} + 4 \operatorname{NH}_3 + \operatorname{O}_2 \longrightarrow 4 \operatorname{N}_2 + 6 \operatorname{H}_2 \operatorname{O} \qquad \Delta_{\mathrm{R}} H^{\circ} = -1632 \text{ kJ mol}^{-1}$$
(R8)

and the thermal decomposition of NO into its elements

$$2 \operatorname{NO} \longrightarrow \operatorname{N}_2 + \operatorname{O}_2 \qquad \Delta_{\mathrm{R}} H^{\circ} = -180 \, \mathrm{kJ} \, \mathrm{mol}^{-1}$$
 (R9)

Over the whole temperature range, nitrogen is the thermodynamically most stable product [7]. Therefore, a catalyst is needed as the non-catalytic combustion of ammonia would exclusively lead to the formation of nitrogen and water. As a result of the high combustion temperatures, the reaction is controlled by external mass transfer. While at low temperatures (200 – 400 °C) nitrogen and especially N₂O are the dominant products, in the mass transfer controlled regime (above 600 °C) the reaction to NO is preferred.

For a medium-pressure reactor operated at around 5 bar, realistic estimates for the product selectivities are 1.5 - 2.5% for N₂O, 1.5 - 2.5% for N₂[9] and 95 - 97% for NO [17].

Catalytic ammonia oxidation on platinum (in this case supported on oxides) also plays a role in automotive catalysis where it is applied in SCR technologies for the removal of overdosed ammonia. In these systems, the operation temperature is in the range 150 - 600 °C, much lower than in industrial ammonia oxidation. Over this temperature range, a transition in the main reaction product is observed from N₂ at low temperatures to N₂O at intermediate and to NO at high temperatures. This transition has been measured and well predicted with a surface kinetic model by [18, 19].

Ammonia production in the Haber-Bosch process is energy-intensive and heavily relying on fossil resources. In combination with the large scale of the Ostwald process, even small improvements in the NO selectivity of the industrial burners allow for significant energy savings and corresponding reductions in CO_2 emissions. Furthermore, N_2O is a greenhouse gas with a global warming potential about 300 times higher than that of CO_2 [9]. In addition, N_2O is the dominant ozone depleting substance among anthropogenic emissions in the 21st century [20]. Due to the environmental impact, regulations and incentives to reduce N_2O emissions have been put into force. Energy savings and the legislation controlling N_2O emissions present a strong motivation to improve the selectivity of industrial ammonia oxidation.

3.2.1. Reactor and operating conditions

The combustion of ammonia is realized in large burning vessels of several meters in diameter [7, 21] and at pressures ranging from atmospheric pressure up to 16 bar. Therefore nitric acid plants can be classified into atmospheric-, medium- and high-pressure plants. Average sized plants exhibit a capacity of 1000 tons pure HNO_3 per day [17], while the larger plants reach capacities up to 2000 t d⁻¹[15]. An overview of the typical process parameters for these three plant types is given in Table 3.1.

With an ammonia conversion of almost 100% and possible NO selectivities up to 98% [15], from a reaction engineers point of view, the oxidation of ammonia is one of the most efficient processes in the chemical industry. Full conversion is needed to prevent the formation of ammonium nitrate (NH_4NO_3) and its deposition in cooler plant sections downstream of the burner, as NH_4NO_3 may cause spontaneous explosions. The feed consists of ammonia vapor and air and is preheated moderately. Limited by the lower explosion limit of ammonia, high-pressure plants can operate with up to 10.5% ammonia while

in atmospheric-pressure systems an ammonia content in the feed of up to 12.5% can be realized, as the lower explosion limit declines with increasing pressure and decreasing flow velocity [15].

Feature		Plant type	
	Low pressure	Medium pressure	High pressure
Pressure / bar	1 – 2	3 – 7	>8
Ammonia content / %	12.0 – 12.5	10.5 – 11.5	10.0 - 10.5
Gas velocity / m s ^{-1}	0.4 - 1.0	1 – 3	2 – 4
Catalyst loading / t $NH_3 m^{-2} d^{-1}$	2 – 4.5	10 - 40	30 – 70
Gauze Temperature / °C	800 - 850	880 - 900	900 – 950
No. of gauzes	3 – 5	6 – 10	20 - 50
Catalyst loss / g t $^{-1}$ N in NH $_3$	0.2 - 0.4	0.7 – 0.9	1.1 - 2.2
Operating time / months	7 – 12	6 – 8	1.5 – 3

Table 3.1.: Typical operating conditions of industrial low-, medium- and high-pressure ammonia burners [21].

The combustion at high pressures leads to a noticeable decrease in NO selectivity [15], but has the advantage of a higher throughput. Due to a higher specific load, higher catalyst temperatures and increased O_2 partial pressures, the loss of precious metals (Pt and Rh) per ton of pure nitric acid increases when operating at higher pressures, so that the catalyst gauzes have to be changed more frequently. Higher mass flow rates also require more catalyst inventory, as the conversion per gauze decreases. Low pressures on the other hand result in a decreasing absorption efficiency in the absorption tower. Therefore, most modern plants are operated in a dual pressure mode, where ammonia is combusted at moderate pressures (4 – 6 bar) while the absorption takes place at higher pressures (9 – 12 bar) [15]. Many authors claim that the drop in NO yield with increasing pressure is due to Le Chatelier's principle, as the equilibrium of reaction R1 is shifted in favor of the reactants if the pressure is increased. Supported by a thermodynamic analysis, Warner claims that the reaction equilibrium is so far on the side of the products, that, from a thermodynamic point of view, a shift in pressure will have no significant effect on the selectivity [16].

Due to large reactor diameters, the reaction proceeds nearly adiabatic, so that the combustion temperature and the temperature of the gas behind the catalyst are determined by the feed temperature and the adiabatic heat release of the reaction. The latter in turn is a function of the ammonia fraction in the feed. In the temperature regime typical for ammonia oxidation, the NO selectivity increases with rising temperature, while N₂O and N₂ formation are less favored. Based on a theoretical study involving the Lewis number Le of the gas, Warner predicted the temperature of the first gauzes to be elevated compared to the adiabatic temperature, due to Le < 1 under conditions present at industrial ammonia oxidation. Throughout the literature, high gas velocities are justified with the suppression of NO decomposition via reaction R8 at short residence times. However, extending the gauze pack with additional layers and adding NO and N2O to the feed, Warner found no significant decomposition of neither NO nor N₂O. As the reaction is controlled by mass transfer, the effect of gas velocity on the gauze temperature is negligible [22]. An increase in velocity reduces the concentration boundary layer and intensifies the flux of ammonia to the catalyst but increases heat transfer from the wire to the same extent so that the two effects cancel each other out. With an analytic model Warner also shows that the product selectivity is a function of the overall mass transfer coefficient. Decreasing gauze loading or utilizing gauzes with larger wire diameters and/or wider mesh openings (open fractional area) will increase mass transfer resitance, resulting in a higher NO and a lower N₂O selectivity [16].

3.2.2. Catalyst

Despite the investigation of a variety of catalyst materials since the beginning of the industrial ammonia oxidation, platinum gauzes have turned out to remain the most suitable catalyst and are almost exclusively used nowadays. Most common are Pt/Rh alloys with a Rh fraction between 5 and 10%. The Rh serves to improve the mechanical stability of the gauzes, to increase the melting point of the alloy and to reduce platinum losses [15]. Furthermore, a beneficial effect of an increased Rh content up to 10% in weight on the NO yield was reported in the literature [23]. Alloys containing Pd showed comparable performance to pure Pt/Rh gauzes [24]. It is claimed that an inclusion of 5 to 10% Pd into the Pt/Rh alloy reduces the losses of Pt [13]. Some authors also report a slightly increased NO selectivity for these gauzes [25] but also a decline in mechanical and thermal stability [21]. Originally, industrial ammonia oxidation was carried out over woven gauzes. In recent decades, the simple woven gauzes have been replaced by knitted gauzes, which exhibit a more complex geometrical structure. A higher NO selectivity, reduction in N₂O formation, as well as an increased mechanical strength have been reported for gauzes with this optimized gauze geometry [26, 27]. According to manufacturers' specifications, the knitted gauzes also offer improved heat distribution along the catalyst, reducing precious metal losses and slowing down deactivation, leading to extended campaign lengths [9]. The world's leading manufacturers of catalyst gauzes for the production of nitric acid are Johnson Matthey, Heraeus and Umicore. Typical wire diameters lie between 60 μ m and 100 μ m. Since the metal losses in the first gauze packs is higher, upstream gauzes often have a greater wire diameter than the ones downstream. Scanning electron microscopy images of a knitted gauze used for industrial application is shown in Figure 3.2a.



Figure 3.2.: Scanning electron microscopy images of (a) knitted gauze (Multiknit) and (b) woven recovery gauze. Source: Umicore.

Efforts have also been made to replace Pt/Rh gauzes by cheaper catalysts made of non-noble metal oxides. So far however their reduced costs do not outweigh the lower ammonia conversion and NO selectivity as well as the increased vulnerability to poisoning. This makes them only profitable, when used in combination with conventional Pt/Rh catalysts, reducing the number of precious metal gauzes [9].

3.2.3. Catalyst reconstruction and recovery

During operation under industrial conditions, the Pt/Rh catalyst wires undergo structural changes. On the grain boundaries of the initially smooth wires, cauliflower-shaped excrescences begin to grow, covering the whole surface already after a short time in operation [28]. Due to this outgrowing structures, the hydrodynamic diameter of the wires expands and the surface area increases. This is accompanied by a gradual loss in mechanical stability of the gauzes, which become progressively brittle towards the end of a campaign. The increased catalytic area leads to a dilution of the species partial pressures at the catalyst surface, explaining (at least in part) the improve in NO selectivity observed during the first days in service [21]. Several authors report the cauliflower-shaped excressences to be most pronounced at the first gauze layers, while the structure of the rear layers remains almost unchanged [29–31]. One explanation for this restructuring process is suggested in [32], involving the formation of gaseous PtO₂, which is formed at surface areas with higher oxygen partial pressure and diffusing to locations where a less oxidative atmosphere is present and where the oxide is subsequently reduced to Pt. Another mechanism suggests temperature gradients on the surface to be the driving force, with PtO₂ formation at hot spots and a deposition on colder spots [28]. Rh also forms its volatile oxide RhO₂ but its vapor pressure is much smaller, leading to gradual enrichment of Rh at the wire surface, especially at the tips of the cauliflower structures [33].

A part of the volatile precious metals are not re-deposited on the gauze, leaving the reactor through the gas phase. This process makes up the greater part of the overall precious metal losses which vary from 0.05 to 0.5 g per ton of nitric acid. Generally, precious metal losses rise drastically with increasing temperature [23]. Mechanical abrasion represents the second, albeit less dominant, route for metal losses. If the gauze structure however is weakened by vaporization of PtO_2 and RhO_2 , abrasion can cause structural damage to the gauze, leading to a significant drop in burner efficiency. Thus, the gauzes have to be replaced in a time interval varying between 6 weeks and 12 months, depending on the operating pressure. Since in high pressure plants ammonia is combusted at higher temperatures, a more frequent exchange of the catalyst is required.

Pt/Rh catalyst gauzes are also utilized for the catalytic conversion of ammonia and methane to hydrogen cyanide in the Andrussow- or the BMA process. Although the processes carried out at much higher temperatures (1100 – 1200 °C), such structural changes of the catalyst are hardly observed during operation and the catalyst exhibits an extended lifetime [34]. This might be explained with the reduced O_2 partial pressure in the reacting gas mixture (the BMA process is even conducted in absence of oxygen), minimizing or preventing the formation of gaseous PtO₂.

Woven catchment gauzes made of Pd are installed inside or downstream of the Pt/Rh gauze pack. Their function is to recover the volatile PtO_2 and RhO_2 and thus reduce precious metal losses throughout the campaign [35]. The captured platinum forms an alloy with Pd and can be recovered after reactor shutdown. Nowadays most of the recovery gauzes contain small amounts of Ni (about 5%), improving their mechanical strength compared to gauzes made from pure Pd. Such systems allow to reduce the precious metal losses from the catalyst by up to 80% for platinum and up to 30% for rhodium [15]. An SEM image of such recovery gauze, which are also called *getter* systems, is shown in Figure 3.2b.

3.2.4. N₂O abatement measures

Due to its negative impact on the stratospheric ozone layer and its high potential as a greenhouse gas, reduction of N_2O emissions has become a central issue for producers of nitric acid and catalyst manufacturers. This is not only due to increasingly stringent governmental regulations, but also driven by the growing public awareness concerning the implications of global warming. With an annual emission of 400 kt N_2O in the Ostwald process, the production of nitric acid, together with the production of



Figure 3.3.: Scanning electron microscopy images of a knitted gauze with structural changes ("cauliflowers"). (a) magnification ×30 and (b) magnification ×300. Source: Umicore.

adipic acid, is largest source of N_2O within the chemical industry [36]. Existing measures and potential technologies to reduce N_2O emissions are described in [9], thus here only a brief overview will be given. Efforts to reduce N_2O emissions into the environment can generally be classified into four categories, named according to the stage of the overall process where those measures are implemented:

Primary measures refer to the prevention of N_2O formation at the stage of the ammonia oxidation reaction. This involves the optimization of process parameters, catalysts and burner design. Modifications of the reactor concepts however are hardly feasible for exisiting plants due to the high additional investment costs. For existing plants, the most promising efforts are geometrical optimization of the Pt/Rh catalyst gauzes to improve NO selectivity [9]. Primary measures are the most sophisticated approach, as they are beneficial in two ways: First they allow for reduction in N_2O emissions. Second, due to the large scale of the process, every mole of NH_3 that is converted to NO rather than to N_2O makes the process more efficient from an economical point of view.

Secondary measures aim at the reduction of N_2O between the NH_3 converter and the absorption tower. In practice they are realized directly downstream of the catalyst gauzes where gas temperatures are high (800 – 950 °C). At these temperatures, N_2O is metastable and homogeneous thermal decomposition can be achieved by increasing the residence time in the burner. In many plants a basket filled with inert Raschig rings is installed directly behind the catalyst for mechanical support of the gauzes and to ensure an equal flow distribution. It is also common practice to replace the bed with a catalyst for N_2O decomposition.

Tertiary measures are located in the tail gas stream downstream of the absorption column. This has the advantage of not interfering with the core stages of the process, i.e. ammonia oxidation and NO₂ adsorption. N₂O removal can be realized with non-selective catalytic reduction (NSCR) for example with H₂ or CH₄ over a Pd/Al₂O₃ catalyst, selective catalytic reduction (SCR) typically over Fe-based zeolithes with light hydrocarbons or ammonia as fuel or via direct catalytic decomposition. An example for tertiary N₂O abatement system is Uhdes EnviNox[®] technology [36].

Quarternary abatement measures are installed after the tail gas expander. Basically they involve the strategies that can be applied as tertiary measures i.e., NSCR, SCR and direct catalytic

decomposition. Being located *end of pipe*, they have the advantage that no additional modifications of the tail gas expander are required.

3.3. Computational fluid dynamics

In order to investigate the interactions between fluid flow and chemical reactions on the surface of the catalyst the velocity-, concentration- and temperature gradients around the catalytic wires need to be resolved. This requires the solution of conservation equations for mass, momentum, energy and chemical species. The equations for mass and momentum are given by the Navier-Stokes (NS) equations. In most applications no analytic solution exists for the resulting coupled system of nonlinear partial differential equations and therefore numerical methods have to be utilized [37].

Computational fluid dynamics (CFD) is a branch of fluid mechanics, that uses numerical methods and algorithms to solve problems concerning the flow of a fluid by evaluating approximate solutions of the governing flow equations. Common numerical methods are the finite volume method (FVM), finite element method (FEM) and finite difference method (FDM). In recent years also Lattice-Boltzmann methods have gained increasing attention, not only due their excellent numerical stability but also because code implementation and parallelization are relatively simple. For most CFD applications, nowadays the FVM is used. Even though FEM is also used to solve fluid mechanical problems, their main application lies in numerical analysis of structural mechanics. One great advantage of the FVM is that continuity is guaranteed for every finite control volume, whereas the FEM yields continuity only over the boundaries of the whole computational domain [38].

The early developments of CFD reach back into the 1960s, where the emergence of more and more powerful computers and algorithms allowed the investigation of systems with increasing complexity. One of the main driving forces behind this development was the aerospace engineering sector. With the birth of commercial jet transport and the upcoming space travel, there was a great need for the extension of the classical aerodynamic experiments by numerical investigations, since many physical phenomena and conditions cannot or only hardly be investigated or realized in an experimental setup, which in most cases was a wind tunnel. The improvement and applicability of CFD codes is closely linked to the development of computers and accessibility to computational power. Therefore, nowadays CFD is used in nearly every domain in which fluid flow is of importance. Examples are the already mentioned aerospace engineering sector, automotive and engine applications, naval architecture, chemical reaction engineering, biological systems, meteorology and many more [39]. Today numerous commercial and open-source CFD codes such as ANSYS Fluent, ANSYS CFX, COMSOL Multiphysics, STAR-CCM+ or OpenFOAM are available, allowing for fast and efficient CFD calculations even on comparatively low priced desktop computers.

The main idea of CFD consists of the transformation of the analytic differential equations into systems of algebraic equations, which can then be solved numerically, either by direct methods, like Gauss method or LU decomposition, or iterative algorithms such as Gauss-Seidel or Jacobi method. A general scheme of a CFD simulation is sketched in Figure 3.4: In a first step the mathematical description of the physical problem has to be set up, i.e. the governing equations have to be defined. All assumptions and simplifications concerning the physical system are made at this stage. The second step consists of defining the physical space (geometry) for which the mathematical problem has to be solved.

The continuous space of the domain is subdivided into a finite number of discrete elements. Inside or on the faces and edges of these elements, so called nodes are defined. The next step involves the discretization of the system of differential equations D into a system of algebraic equations A within the discretized geometry. Finally, the obtained system of algebraic equations is solved and solutions on the nodes are obtained. Thus, instead of finding analytical solution functions A(t, x, y, z) that describe the behavior of a quantity (for example velocity, pressure or temperature) continuously in space and time, approximate values of these quantities $D(t_i, x_i, y_i, z_i)$ are calculated on a finite number of selected points x_i, y_i, z_i within the space and on selected points in time t_i .



Figure 3.4.: General scheme of a CFD simulation.

3.3.1. Governing equations

The flow-, temperature- and concentration profiles throughout the catalyst can be obtained by solving the respective conservation equation. As in these equations the fluid is treated as a continuum, the characteristic length of the domain L must be much smaller compared to mean free path of the gas molecules λ_m , i.e the Knudsen number $Kn \ll 1$, with

$$Kn = \frac{\lambda_{\rm m}}{L} = \frac{k_{\rm B}T}{\sqrt{2\pi\,\sigma_{\rm m}^2\,p\,L}} \tag{3.1}$$

T is the absolute temperature, k_B the Boltzmann constant, σ_m the diameter of the molecules and *p* the pressure. For nitrogen (mean molecular diameter of $\sigma_m = 3.14 \cdot 10^{-10}$ m) at typical combustion conditions T = 1100 K and p = 5 bar as well as $L = 100 \mu m$, which is the typical diameter of a catalyst wire, the Knudsen number can be estimated to $Kn = 6.9 \cdot 10^{-4}$. This is lower than the typical limit of Kn = 0.01, below which the continuum hypothesis can be applied.

The continuity equation of the fluid is given by the following equation:

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \boldsymbol{u}) = 0 \tag{3.2}$$

where ∇ is the nabla operator, ρ the density and u is the velocity vector. For a compressible Newtonian fluid, the momentum conservation equation reads:

$$\rho \frac{\partial \boldsymbol{u}}{\partial t} + \rho(\boldsymbol{u} \cdot \nabla) \boldsymbol{u} = -\nabla p + \mu \nabla \cdot \left[\nabla \boldsymbol{u} + (\nabla \boldsymbol{u})^{\mathrm{T}} - \frac{2}{3} \nabla \cdot \boldsymbol{u} \boldsymbol{I} \right] + \boldsymbol{f}_{\boldsymbol{v}}$$
(3.3)

where μ is the dynamic viscosity of the fluid and I the unit tensor. The second term on the l.h.s. of Equation (3.3) represent the convective transport of momentum and the first two terms on the r.h.s describe pressure forces and diffusive transport of momentum. The vector f_v contains all volumetric forces (e.g. gravitational forces) and is neglected in this work. To avoid confusion, it is emphasized that ∇ denotes the gradient while the divergence is given by ($\nabla \cdot$). Equations (3.2) and (3.3) referred to as the Navier-Stokes equations.

In an typical medium pressure ammonia burner the velocity of the gas upstream of the catalyst lies in the range of 1 m s⁻¹ and is increased up to about 3 m s⁻¹ when passing through the gauze. With Mach numbers lower than Ma < 0.3, even gaseous flow can be assumed to be incompressible [40]. As $Ma \ll 1$ in the system under examination, the governing equations of flow will be used in their incompressible form. If the flow is assumed to be incompressible, the density becomes a parameter and thus Equation (3.2) can be simplified to

$$\nabla \cdot \boldsymbol{u} = 0 \tag{3.4}$$

The incompressible form of the momentum equation is obtained by combining Equations (3.4) and (3.3). Furthermore neglecting the volume forces f_v) one obtains:

$$\rho \frac{\partial \mathbf{u}}{\partial t} + \rho (\mathbf{u} \cdot \nabla) \mathbf{u} = -\nabla p + \mu \Delta \mathbf{u}$$
(3.5)

where Δ is the Laplace operator, which is equal to $(\nabla \cdot \nabla)$. The balance equation for the thermal energy of an incompressible fluid is given by

$$\rho \frac{\partial h}{\partial t} + \rho(\boldsymbol{u} \cdot \nabla)h = \nabla \cdot (\lambda \nabla T) + \nabla \cdot \left(\sum_{i} h_{i} \boldsymbol{J_{i}^{m}}\right) + \dot{S_{h}}$$
(3.6)

 λ is the (isotropic) thermal conductivity, J_i^m the vector of diffusive mass flux of species *i* and S_h an energy source term e.g. due to chemical reactions or radiation. On the r.h.s of Equation (3.6), the first term describes enthalpy transport by convection, while conductive heat transfer and enthalpy transport by species diffusion is given by the first two terms on the r.h.s.. The specific enthalpy *h* of the fluid is calculated from the specific enthalpies of the individual species:

$$h = \sum_{i} \omega_i h_i \tag{3.7}$$

with

$$h_i = \int_{T_{\text{ref}}}^T c_{p,i} \, \mathrm{d}T' + h_i(T_{\text{ref}})$$

where c_p is the specific heat capacity at constant pressure and ω_i the mass fraction of species *i*. Due to the incombressibility of the flow, kinetic energy terms and pressure work as well as viscous heating terms (dissipation) are neglected in Equation (3.6).

In order to resolve the distribution of chemical species within the domain, the balance equation for every species needs to be solved:

$$\rho \frac{\partial \omega_i}{\partial t} + \rho (\boldsymbol{u} \cdot \nabla) \omega_i = -\nabla \cdot \boldsymbol{J}_i^{\boldsymbol{m}} + \dot{S}_i$$
(3.8)

 \dot{S}_i is the source term of species *i*, e.g. due to a chemical reaction. Species transport via convection is represented by the second term on the l.h.s. of the equation, while first term on the r.h.s. describes the

diffusional mass transfer mass transfer. The species diffusive mass flux vector is modeled using Fick's first law:

$$\boldsymbol{J_i^m} = -\rho \boldsymbol{D_{m,i}} \nabla \omega_i \tag{3.9}$$

Here $D_{m,i}$ is the mixture averaged diffusion coefficient of species *i*. In the incompressible form of the NS equation, the density is independent of the flow field and thus becomes a parameter that can be calculated from an equation of state. In this work, ideal gas behavior is assumed:

$$\rho = \frac{p\overline{M}}{RT} \tag{3.10}$$

where \overline{M} is the mean molar mass of the fluid and is calculated from the molar masses of the individual species weighted with the respective mole fraction x_i

$$\overline{M} = \sum_{i} x_i M_i \tag{3.11}$$

In compressible flow, the equation of state is needed to relate the pressure with the density in order to close the NS equations.

These six equations form a closed system of coupled nonlinear second-order partial differential equations (PDE). Since for this system of equations no generalized analytical solution has been found yet, the use of numerical methods is essential solve these equations.

The set of PDEs is solved using the FVM software package Fluent from ANSYS [41]. Since the flow is considered to be incompressible, a density based solver was utilized, with the coupled algorithm for velocity-pressure coupling.

3.3.2. Radiation model

In the industrial process, the oxidation of ammonia is carried out at catalyst temperatures ranging from 800 °C up to 950 °C, depending on the different process parameters, in particular the operating pressure [21]. At these high temperatures, radiative losses can be of importance. They may not only impact the temperature of the catalyst itself, but also influence the temperature of the reactor wall or the distributor plate upstream of the catalyst gauze.

The power per unit area that is radiated from a body with temperature T is described by the Stefan-Boltzmann law:

$$\dot{q}_{\rm rad} = \epsilon \sigma T^4$$
 (3.12)

where σ is the Stefan-Boltzmann constant and ϵ the emissivity, which describes the deviation from a black body radiator. For a black body $\epsilon = 1$, while for a real body $0 < \epsilon < 1$. A body that radiates equally in all directions and for which ϵ is independent of the wavelength of the radiation is called grey body [42].

To describe radiative heat transfer in this work, the so-called Discrete-Ordinate model [41] is used. In this approach, the radiative transport equation is solved as a field equation. Therefore, the full solid angle Ω of 4π is divided into a finite number of discrete angular intervals, each associated with a direction vector *s*, which is the unity normal vector to the area defined by the respective solid angle increment. The resolution of Ω is controlled by the discretization of the azimuth and polar angle. Then, for every *s*, a radiative transport equation is solved at every position **r** in the discretized space:

$$\nabla \cdot (I_{\rm rad}(\boldsymbol{r}, \boldsymbol{s})\boldsymbol{s}) = -(a + \sigma_s)I_{\rm rad}(\boldsymbol{r}, \boldsymbol{s}) + an^2 \frac{\sigma T^4}{\pi} + \frac{\sigma_s}{4\pi} \int_0^{4\pi} I_{\rm rad}(\boldsymbol{r}, \boldsymbol{s'})\Phi(\boldsymbol{s} \cdot \boldsymbol{s'})\mathrm{d}\Omega$$
(3.13)

where *n* is the refractive index of the medium and Φ the phase function. The radiant intensity $I_{\rm rad}$ (W m⁻² sr⁻¹), which for grey radiation is independent of the radiation frequency, is a function of position r and the direction s. The first term on the r.h.s describes the energy losses of a beam of radiation due to absorption and scattering in the medium (a and $\sigma_{\rm s}$ are the absorption and the scattering coefficient). The second and the third term are the contributions due to emission of the gas and due scattering of radiation beams from other directions s'.

The interaction of the gas with radiation, i.e. emission, absorption and scattering, is neglected in this work, thus *a* and σ_s are both set to zero. As a consequence, inside the fluid domain, all contributing terms on the r.h.s of Equation (3.13) are vanishing, and I_{rad} does not change when passing through the gas. Only at the internal boundaries, i.e. the interface between fluid and catalyst, radiation is absorbed or (diffusely) reflected.

3.3.3. Boundary conditions

In the steady state formulation the PDE system defined in Equations (3.4), (3.5), (3.6), (3.8) and (3.10) form a boundary value problem. In order to solve this set of equations, conditions have to be defined for all external and internal boundaries of the domain. At the inlet fixed values for temperature $T_{\rm in}$, velocity vector $u_{\rm in}$ and species mass fraction $\omega_{{\rm in},i}$ are specified. A fixed value for the pressure $p_{\rm out}$ is set at the outlet of the domain. A small representative cuboid section of the catalyst is investigated with the CFD model. Since the radial dimensions of an industrial reactor (in the order of several meters) are very large compared to the scale of the small catalyst section (mm), symmetry boundary conditions are chosen for all external edges (in two dimensions) and faces (in three dimensions) orthogonal to the main flow direction. Mathematically speaking, all convective and diffusive terms normal to that boundary are zero: $u \cdot n = 0$ for momentum, $-\nabla T \cdot n = 0$ for energy and $-J_i \cdot n = 0$ for species transport, where n denotes the unit normal vector of the respective surface element. At the interface between the solid platinum wires and fluid, a no slip condition for the flow (u = 0) is implemented.

To account for chemical reactions occurring at the surface of the catalyst, rates R_i for gas species participating in the respective reactions are calculated from the solution of reaction kinetic models described in greater detail in the individual sections of this work. These source terms are directly coupled with the species balance in the gas phase, as the production/consumption rate of every species must equal its net diffusive flux from/towards the catalyst surface $J_i^m|_s$, which is calculated using Equation (3.9).

$$J_i^m|_{\mathbf{s}} = \boldsymbol{J}_i^m \cdot \boldsymbol{n} = M_i R_i \tag{3.14}$$

 $J_i^m|_s$ is given by the projection of the species diffusion flux vector J_i^m on the unit normal vector n of the respective catalyst surface element. The rates R_i are calculated from the respective kinetic model and are a function of the species mass fractions at the catalyst surface ω_s and the surface coverages θ . As a result of this coupling, the boundary condition requires the simultaneous solution of Equation (3.14) and the respective kinetic model for ω_s and θ_s during each iteration step of the simulation.

The thermal boundary condition at the catalyst surface is given by the balance between the heat release due to chemical reactions and the heat conduction into the gas and the solid catalyst:

$$\lambda_{\rm f} \nabla T|_{\rm s} \cdot \boldsymbol{n} + \lambda_{\rm f} \nabla T|_{\rm s} \cdot \boldsymbol{n} = -\sum_{i} R_i \Delta_{\rm f} H_i^0 \tag{3.15}$$

 $\nabla T|_{s}$ is the temperature gradient evaluated directly at the interface between fluid and catalyst, λ_{f} and λ_{s} are the thermal conductivities of the fluid and the solid catalyst. The standard enthalpy of formation $\Delta_{f}H^{0}$ depends on the temperature and is given by the integral form of Kirchhoff's law:

$$\Delta_{\rm f} H_i^0(T) = \Delta_{\rm f} H_i^0(T_{\rm ref}) + \int_{T_{\rm ref}}^T c_{p,i} \, M_i \, \mathrm{d}T'$$
(3.16)

where the standard enthalpies of formation for the reference temperature $T_{\rm ref} = 298.15$ K are tabulated and taken from [43].

If radiation effects are included in the model, the inlet and outlet boundary are set to behave like black body (Equation (3.12) with ϵ =1) with a temperature equal to that prevailing at the respective boundary. Symmetry at the remaining external edges/faces is achieved by setting these boundaries to specular (total) reflecting surfaces. If s denotes the direction of an incoming ray then the direction of the reflected radiation s_{ref} is given by:

$$\boldsymbol{s}_{\text{ref}} = \boldsymbol{s} - 2(\boldsymbol{s} \cdot \boldsymbol{n}) \cdot \boldsymbol{n} \tag{3.17}$$

The surface of the catalyst is treated as an opaque wall. The radiation energy incident on the surface $\dot{q}_{\rm in}$ can either be reflected (specularly or diffusely) back into the medium or be absorbed. Furthermore the wall surface emits radiation according to its temperature, such that the net radiation energy flux into the surface $\dot{q}_{\rm net}$ can be expressed as:

$$\dot{q}_{\rm net} = \epsilon_{\rm s} \dot{q}_{\rm in} - n^2 \epsilon_{\rm s} \sigma T_{\rm s}^4 \tag{3.18}$$

with ϵ_s being the emissivity of the surface and T_s the surface temperature. The total reflected radiation energy is the sum of specularly and diffusely reflected radiation:

$$\dot{q}_{\rm ref} = f_{\rm d}(1 - \epsilon_{\rm s})\dot{q}_{\rm in} + (1 - f_{\rm d})(1 - \epsilon_{\rm s})\dot{q}_{\rm in}$$
(3.19)

The fraction of the radiation, that is diffusely reflected is defined by $f_{\rm d}$.

3.3.4. Physical properties

In order to describe the physical properties of the flow, heat capacity, viscosity, thermal conductivity and diffusion coefficients need to be defined. These quantities are all functions of temperature and composition. In addition, diffusion coefficients also depend on pressure.

The specific heat capacity c_p , viscosity μ and thermal conductivity λ of the fluid are obtained from the respective species properties using a mass weighted mixing law:

$$c_p = \sum_i \omega_i c_{p,i} \tag{3.20}$$

$$\mu = \sum_{i} \omega_{i} \mu_{i} \tag{3.21}$$

$$\lambda = \sum_{i} \omega_i \lambda_i \tag{3.22}$$

The diffusion coefficient of species *i* in the mixture $D_{i,m}$ can be determined from the binary diffusion coefficients D_{ij} of species *i* and *j*, which is given by:

$$D_{i,\mathrm{m}} = \frac{1 - x_i}{\sum\limits_{j \neq i} \frac{x_j}{D_{ij}}}$$
(3.23)

where x_i is the mole fraction of species *i*.

The species properties are represented in the form of temperature-dependent polynomials. The respective polynomial coefficients for the $c_{p,i}$ and μ_i are taken from [43] and can be found in the appendix. The coefficients for λ_i and D_{ij} are derived from Chapman-Enskog theory [44]:

$$D_{ij} = \frac{3}{16} \frac{\sqrt{2\pi \, k_B^3 \, T^3 \left(\frac{1}{m_i} + \frac{1}{m_j}\right)}}{p \, \pi \, \sigma_{ij}^2 \, \Omega^{(1,1)^*}}$$
(3.24)

with

$$\sigma_{ij} = \frac{1}{2}(\sigma_i + \sigma_j)$$

and

$$\lambda_i = \frac{25}{32} \sqrt{\left(\frac{\mathbf{k}_{\mathrm{B}} T}{m_i \pi}\right)} \frac{c_{v,m}}{\sigma_i^2 \, \mathrm{N}_{\mathrm{A}} \, \Omega^{(2,2)^*}} \tag{3.25}$$

In these equations *m* is the mass of the molecule, N_A Avogadros constant and $c_{v,m}$ the molar heat capacity at constant volume. The reduced collision integrals $\Omega^{(l,s)^*}$ are a measure of intermolecular interaction and depend on the Lennard-Jones parameters ϵ and σ , i.e the well depth of the Lennard-Jones(12, 6) potential and the collision diameter. The collision integrals are calculated with the Lennard-Jones potential for non-polar gases and with the Stockmayer potential for polar gases. Tabulated values for $\Omega^{(l,s)^*}$ can be found in the literature [45–47]. Prior to the polynomial fitting, the Lennard-Jones parameters have been optimized and checked against literature data for binary diffusion coefficients and thermal conductivities. For a detailed description of the procedure see [48]. Tables with the resulting polynomial coefficients for D_{ij} and λ_i are presented in the appendix.

We have investigated industrial NH_3 on Pt catalysts in a different publication [49], where binary diffusion coefficients have been calculated using the method proposed by Fuller [50]. His theory is based on Equation (3.24) but assumes D_{ij} to be proportional to $T^{1.75}$ instead of $T^{1.5}$ as predicted by kinetic gas theory. The intermolecular interaction are hereby described in terms of diffusion volumes which have to be defined for all species within the mixture. They can also be calculated via an incremental method by summing over the atomic and structural contributions of a species molecule. For a detailed description of the model as well as values of the diffusion volumes for some common gaseous species see [50].
3.3.5. Finite volume method

The finite volume method (FVM) is a numerical approach to discretize a set of (partial) differential equations (PDE), that describe the evolution of conserved quantities. Within the FVM, the differential equations are transformed into a system of algebraic equations, that can be solved numerically and thus facilitating the solution of complex physical problems for which in most cases no analytic solution exists [51]. For demonstration purposes a transport equation is considered, where the general scalar ϕ is transported via convection and diffusion:

$$\frac{\partial(\rho\phi)}{\partial t} + \nabla(\rho\phi \boldsymbol{u}) = \nabla \cdot (D_{\phi}\nabla\phi) + S_{\phi}$$
(3.26)

where S_{ϕ} describes a source term. The central idea behind the FVM is to discretize the continuous space into a number of finite control volumes (CV), which is also referred to as meshing, and then to integrate the transport equation for each individual CV over the respective volume $V_{\rm c}$:

$$\int_{V_{\rm c}} \frac{\partial(\rho\phi)}{\partial t} \mathrm{d}V + \int_{V_{\rm c}} \nabla(\rho\phi \boldsymbol{u}) \mathrm{d}V = \int_{V_{\rm c}} \nabla \cdot (D_{\phi} \nabla\phi) \mathrm{d}V + \int_{V_{\rm c}} S_{\phi} \mathrm{d}V$$
(3.27)

Applying Gauss' theorem, the volume integrals over the divergence of the convective and diffusive fluxes can be replaced by an integration of the respective fluxes itself over the surface of the CV:

$$\int_{V_{\rm c}} \frac{\partial(\rho\phi)}{\partial t} \mathrm{d}V + \oint_{A_{\rm c}} \rho\phi \,\boldsymbol{u} \cdot \boldsymbol{n} \,\mathrm{d}A = \oint_{A_{\rm c}} D_{\phi} \nabla\phi \cdot \boldsymbol{n} \,\mathrm{d}A + \int_{V_{\rm c}} S_{\phi} \mathrm{d}V \tag{3.28}$$

Here A_c is the surface of the CV and n is the surface normal vector. Since the flux of the scalar quantity ϕ leaving a CV through a face is equal to the flux entering the neighboring CV through that very same face, the FVM scheme ensures the conservation of ϕ over a CV, arbitrary groups of CVs and thus for the whole domain. Usually, the control volumes are of cuboid, tetrahedral or simple polyhedra shape. Thus the surface integral can be expressed as a sum over the integrals over all surfaces of the CV with little effort. It is common practice to use a first order approximation such as the midpoint rule to discretize the surface and volume integrals:

$$\frac{\partial(\rho\phi)}{\partial t}V_{c} + \sum_{i} \rho_{i}\phi_{i} \boldsymbol{u}_{i} \cdot \boldsymbol{n}_{i} A_{i} = \sum_{i} D_{\phi}\nabla\phi_{i} \cdot \boldsymbol{n}_{i} A_{i} + S_{\phi}V_{c}$$
(3.29)

The index i runs over all surfaces of the control volume and denotes, that the respective quantity is evaluated at the surface. During the solving procedure, the scalar ϕ is stored only at the cell centers, the convective and diffusive fluxes however need to be evaluated at the surfaces of the CV. Therefore, the quantity ϕ needs to be interpolated from the cell centers and discretization schemes for the gradient $\nabla \phi$ need to be defined, which is also called spatial discretization. Having defined descretization schemes for the time derivative (temporal discretization), the PDE has been fully discretized and converted into a system of algebraic equations of the form:

$$\boldsymbol{A} \cdot \boldsymbol{\phi} = \boldsymbol{b} \tag{3.30}$$

where A is a matrix containing all coefficients obtained from the discretization procedure, ϕ the solution vector with the unknown values of ϕ at the center of all control volumes and b is the vector containing all source terms, boundary conditions, non-linearizable terms and constant values. Typically A is a sparse matrix, with the sparsity largely governed by the accuracy order of the discretization schemes used. The size of A is determined by the number of cells in the computational domain, i.e. by the spatial resolution. Thus, in CFD applications A can easily become very large and therefore often iterative methods such as

Gauss-Seidel are more efficient and preferred over direct methods such as L-U-Decomposition. Using an iterative method to solve the system of linear equations in Equation (3.30) and considering that it is only a discretized representation of the PDE, its solution is only an approximation to the analytic solution of Equation (3.26). However, if a sufficiently fine mesh size and appropriate discretization schemes are used, the FVM can yield solutions with a satisfactory degree of accuracy.

3.4. Turbulence modeling

Turbulence flow occurs in a variety of technical and natural processes. In fact, the majority of flows that we observe and experience in our every day life are of turbulent character. In contrast to laminar flow, turbulent flow is characterized by its unsteady random motion and "chaotic" behavior. The formation of turbulence originates from instabilities of the flow field caused by perturbations of the fluid, for example by a static mixer inside a flow tube. The stability against such perturbations is determined by the ratio of inertial to viscous forces, which is characterized by the Reynolds number *Re*:

$$Re = \frac{\rho \, u \, L}{\mu} \tag{3.31}$$

where u is the velocity of the fluid and L is the characteristic length of the body or domain. If Re exceeds some critical value, the flow becomes unstable or turbulent [52]. The value of the critical Re depends on the geometry of the flow and the boundary conditions. Turbulent motion occurs on a large range of spatial and temporal scales, with vortices of many different sizes interacting among each other. In a cascade-like process, kinetic energy is is transferred from large scale eddies, which are typically the size of the physical domain, down to smaller sized structures, until viscous forces become dominant and the kinetic energy is dissipated into heat [52].

Despite being subject to experimental and theoretical investigations for more than a century, turbulent flow phenomena are still not fully understood. Theoretically they are fully contained within the mathematical description of fluid flow given by the Navier-Stokes equations. But due to the chaotic nature of turbulent flow with a broad range of spacial and temporal scales present, huge numerical effort is required to solve the NS equations directly.

3.4.1. Reynolds-averaged Navier-Stokes equations

In general, three categories of simulation methods have been developed for the modeling of turbulent flow differing in their numerical complexity and degree of modeling. The numerically most efficient group of methods can be summarized as *Reynolds-averaged Navier-Stokes* (RANS) simulations. They require the highest degree of modeling and provide a purely statistical description of turbulent flow. An instantaneous scalar quantity ϕ can be decomposed into an average $\overline{\phi}$ and a fluctuating component ϕ' ($\phi = \overline{\phi} + \phi'$). Plugging the decomposed velocity and pressure into the continuity equation (Equation (3.2)) and momentum equation (Equation (3.3)) and performing a time average of the equations, the Reynolds-averaged Navier-Stokes equations are obtained. Using index notation they are given as:

$$\frac{\partial \rho}{\partial t} + \frac{\partial (\rho \overline{u}_i)}{\partial x_i} = 0$$
(3.32)

$$\frac{\partial(\rho\overline{u}_i)}{\partial t} + \frac{\partial(\rho\overline{u}_i\overline{u}_j)}{\partial x_j} = -\frac{\partial\overline{p}}{\partial x_i} + \frac{\partial}{\partial x_j} \left[\mu \left(\frac{\partial\overline{u}_i}{\partial x_j} + \frac{\partial\overline{u}_j}{\partial x_i} - \frac{2}{3}\frac{\partial\overline{u}_l}{\partial x_l}\delta_{ij} \right) \right] - \frac{\partial\tau_{ij}^{\mathrm{R}}}{\partial x_j}$$
(3.33)

The reynolds stress tensor τ_{ij}^{R} is the only term, that is not expressed in terms of time-averaged quantities. To solve the equations, τ_{ij}^{R} must be defined which is the task of RANS modeling. *Eddy-viscosity models* use the Boussinesq hypothesis to relate the Reynolds stress tensor to the mean velocity gradients:

$$\tau_{ij}^{\rm R} = -\rho \overline{u'_i u'_j} = \mu_{\rm t} \left(\frac{\partial \overline{u}_i}{\partial x_j} + \frac{\partial \overline{u}_j}{\partial x_i} \right) + \frac{2}{3} \left(\mu_{\rm t} \frac{\partial \overline{u}_k}{\partial x_k} + \rho k_{\rm t} \right) \delta_{ij}$$
(3.34)

The introduced turbulent viscosity μ_t and turbulence kinetic energy k_t need to be modeled in order to close Equation (3.33). In this work a RANS $k-\omega$ -SST model is used for the initialization of a large eddy simulation, which is described in the next section. For a detailed description of the $k-\omega$ -SST model see [53].

3.4.2. Large eddy simulations

In a *direct numerical simulation* (DNS) the Navier-Stokes equations are solved directly without introducing any turbulence models. In order to correctly resolve the turbulent flow at small length and time scales, very fine computational grids and small time steps are required. This makes DNS computationally very expensive, limiting their application to a few special cases of low *Re* flow [52].

Large eddy simulations (LES) provide a trade-off between the high degree of modeling in a RANS simulation and the large computational effort of a DNS. In a LES only larger sized eddies, which contain most of the turbulent kinetic energy, are resolved, while smaller sized eddies are modeled using a so-called subgrid-scale model. The separation is realized using a filter operation. Many CFD codes employ an implicit filtering approach, in which the computational grid itself is acting as a filter:

$$\overline{\phi}(x) = \frac{1}{V} \int_{v} \phi(x') dx', \quad x' \in v$$
(3.35)

where V is the volume of a computational cell. The filtered conservation equations for mass and momentum are then given by

$$\frac{\partial \rho}{\partial t} + \frac{\partial (\rho \overline{u}_i)}{\partial x_i} = 0$$
(3.36)

$$\frac{\partial(\rho\overline{u}_i)}{\partial t} + \frac{\partial(\rho\overline{u}_i\overline{u}_j)}{\partial x_j} = -\frac{\partial\overline{p}}{\partial x_i} + \frac{\partial}{\partial x_j} \left[\mu \left(\frac{\partial\overline{u}_i}{\partial x_j} + \frac{\partial\overline{u}_j}{\partial x_i} - \frac{2}{3}\frac{\partial\overline{u}_l}{\partial x_l}\delta_{ij} \right) \right] - \frac{\partial\tau_{ij}^{\text{SGS}}}{\partial x_j}$$
(3.37)

The filtered quantities are denoted by an overbar and represent the resolved part of the fluid, leaving only the subgrid reynolds stress tensor τ_{ij}^{SGS} to be modeled using a suitable subgrid-scale model.

$$\tau_{ij}^{\text{SGS}} = \rho \overline{u_i u_j} - \rho \overline{u}_i \overline{u}_j \tag{3.38}$$

In this work the *dynamic kinetic energy subgrid-scale model* was used for the statistical description of the subgrid-scale turbulence. The model and its implementation in ANSYS Fluent is described in [53].

4. Literature Overview

4.1. Mass transfer correlations

At temperatures relevant for industrial ammonia oxidation, the reaction over the Pt catalyst is controlled by external mass transfer. Literature reports, that at temperatures above 600 °C the reaction rate at the surface becomes so fast, that the overall rate of the reaction is determined by the diffusion of reactants towards the surface of the catalyst. This was already reported by Andrussow[54]. Warner points out, that despite the knowledge of its existence, many researchers ignored these mass transfer limitations when determining the conditions for their (kinetic) experiments and investigations [16].

In order to simplify the studies, the complex woven and knitted gauzes are frequently replaced by simpler geometric bodies, such as isolated wires or stacks of wires. Heat and mass transfer from cylinders in cross flow of gases and liquids has been studied intensively for a broad range of *Re* and numerous correlations are proposed [42, 55].

It is common practice to relate data obtained from heat transfer experiments to mass transfer correlations using the Chilton-Coleburn j-factor analogy [56]:

$$j_h = \frac{Nu}{Re P r^{1/3}} = j_m = \frac{Sh}{Re S c^{1/3}} = j$$
(4.1)

with j_h and j_m the j-factors for heat and mass, Pr the Prandtl number and Sc the Schmidt number. The Nusselt number Nu quantifies the ratio of convective heat transfer to heat transfer by conduction and is defined as

$$Nu = \frac{\alpha L}{\lambda} \tag{4.2}$$

with α being the heat transfer coefficient and *L* the characteristic length. Its mass-transfer-analogue is the Sherwood number *Sh*, which is the ratio of convective mass transfer to mass transfer by diffusion, defined as

$$Sh = \frac{\beta L}{D} \tag{4.3}$$

with β being the mass transfer coefficient. For a single cylinder, most authors suggest a j-factor in the form of:

$$j = C_1 \, R e^{m-1} f\left(Pr\right) \tag{4.4}$$

with C_1 being a constant depending on the regime of Re. The parameter m is also a function of Re and is ranging between 0.3 and 0.4 for low Re flow, with Re being calculated using the free stream velocity and the cylinder diameter as characteristic length. As a consequence, the Sherwood number of a cylinder in cross flow is proportional to Re^m . A single comprehensive equation of different form, covering a wide range of Re, is given by [57].

For a bank of tubes in cross flow, the following j-factor is proposed by Zukauskas [58]:

$$j = C_2 C_1 R e^{m-1} f(Pr)$$
(4.5)

Here the maximum velocity throughout the bank is used for the calculation of Re. For a bank of cylinders, C_1 depends also on the configuration of the cylinders in the stack and C_2 is a correction factor when dealing with only a few rows of cylinders. As in the case of a single cylinder, for low Re flow, a value of ≈ 0.4 is proposed for m. A collection of different correlations for single cylinder and multi-cylinder configurations can be found in [42].

A great number of studies have been dedicated to the investigation of mass transfer characteristics of gauzes and metal screens. A detailed review of mass transfer correlations for gauzes or metal screens is presented in [16] and thus only a short overview is given in this work.

In order to derive correlations, gas phase studies have been carried out using catalytic decomposition or combustion reactions [59–61] and mercury evaporation [62]. Furthermore, mass transfer correlations have been derived from heat transfer experiments using the Chilton-Coleburn analogy [63, 64]. Electrochemical methods have been applied for investigations involving liquid phase flow [65–69], which have shown good agreement with the experimental results from their gas phase counterpart. Heat and mass transfer of woven and knitted gauzes have recently been studied by Kolodziej et al. [70, 71]. The resulting correlations are based on a model assuming laminar flow in a short circular capillary channel. However, the agreement with experimental data from their work, as well as data from other studies is poor.

To establish a functional dependence between the Reynolds number and a j-factor, London suggested the use of the packed bed model, where the mass transfer characteristics of a gauze are assumed to be equal to those of a packed bed [63]. Here the Reynolds number is defined in terms of the hydraulic diameter $d_{\rm h}$ of the bed:

$$Re = \frac{d_{\rm h} \, u_{\rm s} \, \rho}{\mu} = \frac{4\Phi \, u_{\rm s} \, \rho}{a_{\rm s} \, \mu} \tag{4.6}$$

with

$$d_{\rm h} = \frac{4\Phi}{a_{\rm s}} \tag{4.7}$$

where u_s is the superficial velocity, Φ the porosity (or void fraction) of the gauze pack and a_s the surface area to volume ratio.

The use of an infinite cylinder model for this task is proposed by both Satterfield and Shah [60, 61]. For the definition of Re, Satterfield scaled the superficial velocity with the porosity of the gauze pack and chose the wire diameter d_w as characteristic length. For the Chilton-Coleburn j-factor he suggested the following relation:

$$j_{\epsilon} = 0.865 R e_{\Phi}^{-0.648} \quad 0.4 < R e_{\Phi} < 9 \tag{4.8}$$

with

$$Re = \frac{d_{\rm w} \, u_{\rm s} \, \rho}{\mu \, \Phi} \tag{4.9}$$

Shah divided the superficial velocity by the fraction of the open area γ and obtained the following expression for the Reynolds number:

$$Re = \frac{d_{\rm w} \, u_{\rm s} \, \rho}{\mu \, \gamma} \tag{4.10}$$

The resulting correlation proposed by him is given by:

$$j_{\gamma} = 0.644 R e_{\gamma}^{-0.570} \quad 5 < R e_{\gamma} < 245 \tag{4.11}$$

Using Equation (4.1) it can be seen that for both correlations, the Sherwood number, and thus the mass transfer coefficient for a catalyst gauze, is again proportional to Re^m with $m \approx 0.4$. Warner has shown that with the correlation of Shah, a much better fit of the experimental data was obtained compared to the packed bed model. He preferred to use Equation (4.11) over the correlation given by Satterfield, as it was validated over a wider range of conditions. Using evaporation of naphtalene, Voß and Dübler have investigated mass transfer characteristics of both woven and knitted gauzes for industrial ammonia oxidation [72]. They fitted their data into a correlation using the packed bed approach and reported good agreement with the data of London and Satterfield. Assuming a mass transfer controlled reaction, such simplified correlations for the mass transfer characteristics of gauzes have been intensively used throughout the ammonia oxidation literature and in industrial practice, e.g. to determine overall reaction rates, ammonia conversions or to estimate the required catalyst equipment [73–75].

4.2. Kinetic models for ammonia oxidation

Since the early days of the Ostwald process, researchers have tried to elucidate the involved chemical species and the underlying mechanisms of the ammonia oxidation reaction. Complex mechanistic models have been developed proposing intermediates such as nitroxyl [54], imides [76] and hydroxylamine [77].

With more advanced surface science techniques and spectroscopic methods, researchers were able to disprove the early mechanisms and the involvement of the suggested species [78–80]. In ultra-high vacuum studies on Pt single crystal or polycrystalline surfaces they were able to determine most of the elementary steps contributing to the overall reaction. More recently, the reaction mechanism has also been studied by quantum chemical methods [10, 81, 82]. Today, the discussion seems to have converged towards a mechanism which is schematically depicted in Figure 4.1. A very detailed overview of the individual elementary steps is given by Warner [16].



Figure 4.1.: A schematic representation of the generalized reaction mechanism leading to the formation of NO, N₂ and N₂O. "g" denotes a the gaseous species, "s" a species adsorbed at the surface of the catalyst.

In a first step, ammonia is adsorbed on the platinum surface and the adsorbed ammonia is activated by successive abstraction of H-atoms by O(s) and OH(s) (the "s" denotes the the species is adsorbed at the catalyst surface). In this way, adsorbed N atoms N(s) are formed. The selectivity of the reaction is determined by the reaction path followed by these N atoms: Reaction with O(s) yields NO. The recombination of two N(s) results in the formation of N_2 and the reaction with an adsorbed NO molecule NO(s) yields N_2O . In this picture, the selectivity of the process is determined by the relative rates of the reaction paths of the adsorbed N atom to the three products and by the surface coverages of O(s), N(s) and NO(s), which are in turn determined by the gas phase concentrations.

Even nowadays research on surface chemistry seems to ignore the fact that the reaction is mass transfer controlled. Although early works, for example by Schmidt and coworkers, have considered external mass transfer when validating their global kinetic models [83, 84], recent DFT-based reaction mechanisms have been evaluated at bulk gas phase conditions, ignoring any mass transfer effects [10, 11, 82]. There is still only little work published in the literature, where kinetic models have been validated under mass transfer limited conditions.

In early studies of chemical kinetics for industrial ammonia oxidation, simple global mechanistic models [84–87] have been used and the formation of N_2O was neglected. However, the detailed knowledge of the surface mechanism has led to the development of a variety of mean-field microkinetic models during the last 20 years. In the following sections these models will be presented briefly.

4.2.1. Scheibe

The kinetic model of Scheibe was developed for two stepped Pt(111) surfaces, i.e. Pt(533) and Pt(443) [79, 88]. Experiments were conducted at ultra-high-vacuum conditions between 10^{-5} and 10^{-4} mbar and in a temperature range from 450 to 1100 K. Since under these conditions no production of N₂O was observed, the model does not contain reactions describing N₂O formation. The mechanism consists of six gas and six surface species and twelve elementary reactions with individual parameters for both surfaces. The parameters are mostly taken from literature. Being validated only for very low pressures and due to the lack of an N₂O formation reaction, this reaction mechanism is hardly suitable for the investigation of ammonia oxidation under industrial conditions.

4.2.2. Rafti

Rafti developed a model for ammonia oxidation kinetics on a Pt(533) surface [89]. The mechanism is an extension of the Scheibe model, containing a reaction describing N_2O formation. Kinetic parameters were taken from literature, derived from experiments at up to 0.1 mbar and from DFT calculations. Based on this data, the parameters of some elementary steps were refitted. The mechanism exhibits 13 reactions, six reversible and seven irreversible steps, as well as five gas and seven surface species. Although the model contains N_2O formation and is validated at pressures about three orders of magnitude higher than the original Scheibe mechanism, the pressure range is still far from industrial applications. Another drawback arises from some special formulations of the kinetic model, i.e. a certain fraction of surface sites is reserved for oxygen and O_2 and NO coverages are limited to certain threshold value. These features hamper its implementation into standardized kinetic software.

4.2.3. Rebrov

Based on experimental data from a microreactor, Rebrov developed a kinetic model on a polycrystalline platinum surface [78]. The mechanism contains 13 reactions with six gas and five surface species and suggests two different adsorption sites. Experiments were conducted at atmospheric pressure and in a temperature range between 523 and 673 K with short residence times of 0.3–0.7 ms. The fitting of the kinetic parameters was carried out in a two-step process: An isothermal plug-flow-reactor was used for a least-square regression analysis to obtain a first estimate for the parameter set. Using a full CFD model of the microreactor, the kinetic parameters were then further adjusted, until reproducing the experimental data. Although carried out in a temperature range still far below industrial applications,

this was the first attempt of developing a kinetic model using an appropriate reactor model able to resemble mass transfer limitations.

4.2.4. Traversac

Traversac suggested a microkinetic model for ammonia oxidation on a Pt(111) surface, comprising of 22 reversible elementary steps with seven gas and ten surface species [90]. The chosen elementary steps and their kinetic parameters are entirely based on literature data except for the reaction describing N₂O formation/decomposition which was fitted to his experimental results. The model is formulated in a thermodynamic consistent manner, i.e. it is parametrized only for the forward reactions, while the rate constants for the reverse reactions are calculated from the forward rate constants and the equilibrium constant of the respective reaction. Thermodynamic data for gas species was taken from the Abo ÅA database [91], for the surface species it was calculated using expressions from statistical thermodynamics with the respective parameters taken from NIST database [92]. Experiments were conducted in a tubular platinum reactor at atmospheric pressure and temperatures between 200 and 1000 °C with the feed containing 1000 ppm of ammonia. The mechanism was validated against the experimental data using a combined reactor model consisting of a plug-flow reactor, a shear-layer flow reactor and a continuously stirred tank. Traversac also accounted for gas phase reactions, implementing a large kinetic model from [91]. The microkinetic model from Traversac will be used in this work for the investigations in chapter 6, where more details of the mechanism will be presented.

4.2.5. Kraehnert

Kraehnert and Baerns conducted kinetic experiments in a micro-structured quartz-reactor using polycrystalline Pt foil as a catalyst [80]. The investigations were carried out at temperatures between 286 and 385 °C and partial pressures of NH₃ and O₂ up to 6 kPa. Starting from the mechanistic models suggested by Scheibe et al. on a Pt(533) surface, Rebrov on Pt/Al₂O₃ and a third one on Pt(111) proposed by the authors, a parameter fitting was conducted. Of the three models, the one for Pt(111) was discriminated to yield the best fit to the experimental data. It features two different adsorption sites for six gas and six surface species and contains a total of ten elementary reactions. The model has been successfully used to describe ammonia oxidation in exhaust gas after-treatment [18, 93]. Implemented into advanced reactor simulations for ammonia oxidation at medium-pressure conditions, the kinetic model is also able to correctly reproduce the selectivity trends found in industrial practice [22, 94]. This model is used for the studies in chapter 5 and is described in greater detail there.

4.2.6. Novell-Leruth

Derived from DFT calculations, Novell-Leruth et al. proposed a comprehensive microkinetic model for a Pt(100) surface [82]. A full and a simplified version of the mechanism are presented. While the first contains 26 reversible reactions with seven gas and twelve surface species, the simplified model comprises of 14 reactions, of which nine are reversible, six gas and eleven surface species. For both models, two different adsorption sites are assumed. Klingenberger successfully implemented the kinetic model into a CFD reactor simulation, thus accounting for mass transfer limitations [94]. The results however were not in line with experimental findings and industrial experience.

4.2.7. Ma

Recently and also entirely based on DFT calculations, Ma and Schneider developed a model describing kinetics of ammonia oxidation on a Pt(211) as well as a Pt(111) surface [10]. A different parameter set is presented for each of the two surfaces types. The mechanism considers a total of 15 reversible elementary reactions with six gas and ten surface species, featuring thermodynamic consistency for all adsorption/desorption steps. They presented also an extended version of the model with five additional reversible steps, describing further details of the ammonia activation and surface water formation. Using a continuously stirred tank reactor, a zero conversion model and furthermore conducting a degree of rate control analysis, the authors investigated the derived kinetics for conditions prevailing in exhaust gas after-treatment as well as in industrial ammonia oxidation. However, for the latter application the presence of mass transfer limitations was neglected and gas phase concentrations similar to those at the inlet of an industrial burner were utilized.

4.3. Modeling of industrial ammonia oxidation catalysts

Throughout the literature, several models have been used to investigate the combustion of ammonia under industrial conditions. Most of the older work incorporates mass transfer limitations in form of simple transport correlations. Roberts and Gillespie used a unit transfer concept and mass transfer correlations for stacked metal screens from Shah, as well as from Satterfield and Cortez, to predict the amount of required catalyst in a burner [74]. Nutt et al. investigated ammonia conversion along flat Pt-ribbons, round wires and gauze pads with a simple cascade model using different mass transfer coefficients for NH₃ and O₂ derived from boundary layer theory [75]. Hickman et al. [95] and Fíla [96] both developed plug flow models to predict the axial temperature gradients and concentration gradients of NO and N₂ throughout the gauze pack. The latter used heat and mass transfer correlations based on the work of Satterfield and Cortez. Hickman assumed the catalyst and the wire to be in thermal equilibrium and the overall reaction rate was limited by the flux of reactants to the surface given by the Hertz-Knudsen equation. As Warner already pointed out, all these models have in common that they neglect the formation of N₂O and additionally suffer from either not considering the transfer of NO from the surface to the bulk, or using the same mass transfer coefficients for all species. Taking kinetic expressions from the detailed surface kinetic model proposed by Traversac and using the j-factor correlations proposed by Shah, Warner developed analytical expressions for N2 and N2O selectivity ("Master Plots"), overcoming the drawbacks stated above. The model predictions showed good agreement with his experimental data, as well as data from other studies over a broad range of conditions relevant for industrial ammonia oxidation [16]. With this model, Warner was able to give an explanation for the decrease in NO selectivity with increasing pressure and claimed the N₂ selectivity to be a function of the mass transfer coefficient and thus catalyst geometry and gauze loading.

More recent work is focused on treating mass and heat transfer intrinsically, which requires solving the Navier-Stokes equations, as well as the transport equations for heat and species around geometrically resolved gauze structures. No transfer coefficients are needed and spatially resolved boundary layers for velocity, temperature and concentration are obtained. This is done employing CFD codes, which is becoming increasingly popular due to the increasing availability of powerful computational hardware. Nowadays, even more advanced models with complex geometrical catalyst shapes can be investigated on comparatively inexpensive machines. CFD simulations of heterogeneous catalyzed reactions other than ammonia oxidation have been conducted in [97–100]. Studies of hydrogen/air mixtures past an array of catalytic wires [101] and catalytic partial oxidation (CPO) of methane over Pt catalyst gauzes [102] have also been reported in the literature.

Jess and Wasserscheidt investigated ammonia oxidation on an isolated two-dimensional Pt wire using the commercial FEM solver COMSOL [7]. Employing a simplified model for ammonia consumption on the wire surface, the results showed varying heat and mass transfer coefficients along the circumference of the wire. The calculated average transfer coefficients were reported to be in good agreement with analytical expressions derived from *Nu* and *Sh* correlations. A more advanced approach was undertaken by Nien, who implemented the detailed surface kinetic model, published by Kraehnert, into CFD calculations of two- and three-dimensional gauze catalyst models [22]. The implementation of kinetics was efficiently realized using multivariate tensor product spline interpolation of pre-calculated and tabulated rate data as reported in [103]. This spline tabulation approach has already been successfully applied for the description of ammonia slip catalysts in automotive exhaust gas treatment systems [19, 93, 104]. Performing a parameter study including variations of wire diameter and wire configuration, Nien showed the product selectivities to strongly depend on the catalyst geometry.

A similar approach was conducted by Klingenberger, who coupled CFD simulations with a more complex kinetic model derived from DFT calculations by Novell-Leruth [94]. Instead of the conventional tensor product splines utilized by Nien, he used reduced multivariate Hermite Splines which are more efficient in terms of storage requirements and execution time, especially for chemical mechanisms with a large number of elementary steps and chemical species [105]. Klingenberger demonstrated, how resolved reactor simulations, combined with detailed surface kinetics, can be used to validate and tune suggested mechanistic models under mass transfer limited conditions.

4.4. Sensitivity analysis of surface kinetic models

Sensitivity analysis for investigating the characteristics of chemical kinetics is commonly applied in the field of gas phase and surface chemistry. It provides information on the sensitivity of overall reaction rates towards kinetic parameters such as activation energies, pre-exponential factors or sticking coefficients. Such studies are used to identify relevant elementary reaction steps and pathways, allowing to reduce the complexity of mechanistic models. Sensitivity analysis can also guide experimental work by identifying kinetic parameters that need to be measured more carefully. Furthermore, it can assist in the design of experiments and parameter identification for data fitting and model adjustment [106]. It can also be used to evaluate the robustness of predictions made by kinetic models [107]. For a detailed description and overview of general methodologies for sensitivity analysis of chemical kinetic systems, the reader is referred to [106–108].

The increase in available computational power allows to apply sensitivity analysis to larger and more complex kinetic systems, making them a popular and powerful tool to connect reaction kinetic modeling with experimental studies.

In a general sense, the sensitivity of the *j*th entry of the solution vector F (which can be a chemical rate, a concentration or a surface coverage) of the kinetic system with respect to the *i*th parameter of the parameter vector P, such as rate constants, activation energies and temperature, is given by the *normalized sensitivity coefficient* $SC_{i,j}$:

$$SC_{i,j} = \frac{P_i}{F_j} \frac{\partial F_j}{\partial P_i}$$
(4.12)

The sensitivity coefficients can be determined using *brute force* methods, involving perturbation of one parameter, solving the kinetic equations and observing the effects upon the output of the solution. More sophisticated techniques involve the calculation of the systems *Jacobians* or the *green function method* [108].

The concept of a rate-determining step is commonly utilized in analysis of chemical reaction mechanisms [109–111]. It has been broadly used to derive analytic expressions for steady state net rates of surface kinetic systems [112, 113]. Dumesic used *DeDonder* relations to assess the rate-determining step of a mechanistic model [114], while Campbell proposed the more generalized concept of *degree of rate control* for this task [109, 115]. He defines the degree of rate control of step *i* as:

$$X_{\text{RC},i} = \frac{k_i}{R} \left(\frac{\partial R}{\partial k_i}\right)_{k_{l\neq i}, K_{\text{eq},i}}$$
(4.13)

where R is the net production/consumption rate for the species of interest and k_i the rate constant of the *i*th elementary step. The derivative is evaluated keeping the chemical equilibrium fixed (this is achieved by changing the forward and reverse rate constant of reaction *i* by the same factor) and fixing all other rate constants. This expression is of the form of the more general normalized sensitivity coefficient $SC_{i,j}$ in Equation (4.12) but forward and reverse rate constant are not independent parameters, as they are perturbed in the same manner. Thus thermodynamic consistency is maintained, providing the degree of rate control with a deeper physical meaning. The $X_{\text{RC},i}$ quantifies the percentage of increase in the net rate R per percent increase in the rate constant of elementary step *i*.

Campbell proposed the steps with a positive degree of rate control to be called *rate-limiting* steps, while those with a negative value are labeled *inhibition* steps. A rate-determining step is identified by having a $X_{\text{RC},i} = 1$, while the degree of rate control for all other steps would be zero. Especially for larger mechanisms, several steps can have a non-negative degree of rate control, with some steps being more rate-limiting than others. However, it is observed that for most kinetic models only a few elementary steps exhibit $X_{\text{RC},i} \neq 0$ [116]. The degree of rate control allows to identify steps where an increase or decrease in rate constant would be beneficial for the overall rate of the product species, and thus pointing out where catalyst improvement would be beneficial.

The degree of rate control has been frequently used to analyze first principle [10, 11, 117, 118] or experimentally derived [119, 120] microkinetic models, as well as for computational catalyst screening [121]. Later Stegelmann and Campbell extended this concept by replacing the kinetic constants of Equation (6.17) by standard-state free energies, entities stating a deeper physical meaning and easier to control, when thinking of catalyst optimization. They introduced the *general degree of rate control*, which quantifies how much a differential change in standard-state free energy of a transition state or a surface intermediate affects the net rate of the overall reaction[122]. Nørskov, Bligaard and Kleis proposed a further extension of the generalized degree of rate control, by defining the so-called *degree of catalyst control*, which quantifies the impact of any independent catalyst descriptor, such as adsorbate binding energies [123]. Another derived concept based on Equation (6.17) is the *scaled degree of rate control* approach. It combines the degree of rate control analysis with linear scaling relations between transition-metal surfaces in order to investigate rate- and selectivity-controlling elementary steps on different catalyst materials [124].

5. Investigation of industrial ammonia oxidation

5.1. Introduction

Industrial ammonia oxidation has been recognized to be a mass transfer controlled process for almost a century. Despite considerable research efforts invested in the understanding of the surface chemistry and the development of kinetic models, to date the interaction between mass transfer and the surface chemistry has been investigated and discussed only insufficiently.

To this end, two-dimensional steady state simulations of gauze catalysts for ammonia oxidation are presented in this chapter. The computation of flow-, temperature- and species concentration fields around the platinum wires is combined with a detailed description of the chemistry on the catalyst surface by means of a microkinetic model. This allows to study the effect of the flow field around the catalyst on the chemical kinetics and thus the local distribution of product selectivity on the catalyst surface.

In a first step, the flow over a single wire is studied, investigating the effect of gas velocity, wire diameter, wire spacing and surface area. Subsequently, simulations of multiple rows of parallel wires are carried out. These simulations allow to investigate the effects of flow field, catalyst geometry, pressure and radiation losses on the temperature of the catalyst wires and the performance of the process, which according to literature, is still not completely understood. The main focus lies on the N₂O selectivity predicted by the model and on investigating, to what extent currently established kinetic models are able to reproduce the reaction behavior observed in industrial reactors. Current mechanistic models are derived from DFT calculations, surface science experiments or kinetic experiments, conducted either at low pressures or low temperatures. Experiments to obtain kinetic data at industrial relevant conditions are difficult to set up, due to the high exothermicity of the reaction and harsh reaction conditions, as well as the unavoidable mass transfer limitations. Therefore, validation of existing mechanistic models under realistic operating conditions by detailed reactor simulations is an important step in the development and optimization of kinetic models. As the industrial process exists for over a century and due to the long-term campaigns, the industrial experience is an important source of information for the validation of current kinetic models, especially in the absence of the respective data from direct kinetic measurements.

First simulations coupling flow and detailed surface chemistry to study single and multi-wire Pt catalysts for industrial ammonia oxidation have already been conducted by Nien [22] and Fadic [125]. Although in parameter studies they demonstrated the local N_2O selectivity to be sensitive to the flow field and catalyst geometry, they did not elucidate the underlying interplay between flow field, temperature, mass transfer rates of reactants and surface kinetics on a level of detail that is given in this work.

5.2. Computational model

5.2.1. Microkinetic model from Kraehnert

In order to describe the chemical reactions occurring at the surface of the platinum catalyst, the mechanistic model published by Kraehnert [80] is used. It consist of ten elementary reactions, six surface and six gas species. The kinetic parameters can be found in Table 5.1.

 Table 5.1.: Microkinetic model for ammonia oxidation proposed by Kraehnert [80]. Two different adsorption sites on the platinum surface are assumed, denoted by "a" (hollow site) and "b" (top site).

Reaction	Reaction equation	k_0 / s ⁻¹	$E_{ m a}$ / kJ mol $^{-1}$	b
R1	$NH_3 + b \rightarrow NH_3-b$	$1.95 \cdot 10^2$	0.0	1
R2	$NH_3-b \rightarrow NH_3 + b$	$5.45 \cdot 10^9$	60.9	0
R3	$O_2 + 2 a \rightarrow 2 O-a$	$8.99\cdot 10^1$	0.0	1
R4	$2 \text{ O-a} ightarrow ext{O_2} + 2 ext{ a}$	$9.37 \cdot 10^8$	181.0	0
R5	$\rm NH_3\text{-}b$ + 1.5 O-a \rightarrow N-a + 1.5 H_2O + 0.5 a + b	$1.72\cdot 10^{15}$	99.5	0
R6	$NO-a \rightarrow NO + a$	$8.87\cdot10^{16}$	155.0	0
R7	NO + a \rightarrow NO-a	$8.84 \cdot 10^6$	63.5	1
R8	$2 \text{ N-a} \rightarrow \text{N}_2 + 2 \text{ a}$	$2.56\cdot10^{17}$	139.0	0
R9	$N-a + O-a \rightarrow NO-a + a$	$1.93\cdot 10^{16}$	135.0	0
R10	$\text{NO-a} + \text{N-a} \rightarrow \text{N}_2\text{O} + 2 \text{ a}$	$4.00 \cdot 10^{17}$	155.0	0

 k_0 is in m³ s⁻¹ mol⁻¹ K⁻¹ for R1, R3 and R7.

The model applies the mean-field approximation, which assumes that the adsorbed species are homogeneously distributed over the surface, which itself is modeled to be uniform [126]. The rates for the individual elementary steps are calculated as:

$$r_j = k_{0,j} T^b \exp\left(-\frac{E_{\mathrm{a},j}}{\mathrm{R}T}\right) \prod_i c_i^{|\nu_{ij}|} \prod_i \theta_i^{|\nu_{ij}|}$$
(5.1)

where c_i is the concentration of gas species i, θ_i is the surface coverage of surface species i and ν_{ij} the stoichiometric coefficient of species i in reaction j. $E_{a,j}$ is the activation energy, $k_{0,j}$ the pre-exponential factor and b the temperature exponent. The overall rate R_i of a gas or surface species is described by the sum over all individual elementary reactions in which this very species participates:

$$R_i = \Gamma F_{\Gamma} \sum_j \nu_{ij} r_j \tag{5.2}$$

For the site density Γ , a value of $2.71 \cdot 10^{-5}$ mol m⁻² is used. F_{Γ} is a surface enlargement factor, accounting for the difference between the geometrical and actual surface area of a platinum wire due increase in surface area observed in the industrial praxis [30, 31]. It was set equal to 10 in the frame of this work. To obtain the surface coverages, the following system of ordinary differential equations (ODE) is numerically integrated until the desired time *t* is reached:

$$\frac{\mathrm{d}\theta_i}{\mathrm{d}t} = \frac{R_i}{\Gamma} \tag{5.3}$$

In steady state, the left-hand-side of Equation (5.3) becomes zero, resulting in a system of non-linear algebraic equations:

$$\frac{R_i}{\Gamma} = 0 \tag{5.4}$$

The steady state surface coverages are obtained either by solving Equation (5.4) or by integrating ODE system in Equation (5.3) for a sufficiently long time, until steady state is reached. For analyzing the kinetic model, the latter approach was realized in this work, using the numerical solver IDAS from a MATLAB implementation of the SUNDIALS package [127].

5.2.2. CFD model

To investigate the interaction of laminar flow and chemical surface reactions at the scale of the platinum catalyst gauzes, two-dimensional steady state simulations of a gauze catalyst have been set up. During the simulation, the balance equations of mass, momentum, energy and species presented in Equations (3.4), (3.5), (3.6) and (3.8) are solved. The catalyst wires are represented as cylinders with a diameter of $d_w = 100 \mu m$. The chosen diameter is slightly larger than the initial size of the wires used in industrial applications. This takes into account the larger hydrodynamic diameter due to surface restructuring effects during operation leading to the formation of the typical cauliflower-shaped structures [29, 31, 32].

Initially, the reaction over a row of parallel wires, oriented perpendicular to the flow, will be studied. Due to the symmetry of the configuration, only a single wire needs to be considered in the simulations as presented in Figure 5.1. The parameter D determines the center-to-center distance between two wires. The computational mesh consists of triangular cells in the fluid domain and prism shaped layers have been introduced near the wires to improve the resolution of expected gradients.





Figure 5.1.: Left: Geometry of a row of parallel wires perpendicular to the flow. Due to symmetry, only the domain inside the dashed rectangle is considered in the simulations. d_w denotes the diameter of a wire and D is the center-to-center distance between the wires. Right: The respective mesh of the computational domain.

The resulting computational domain is 0.3 mm in height, 0.6 mm in length and contains \approx 5600 mesh elements. Grid independence of the solution was studied by roughly doubling the number of mesh elements and comparing the N₂O mass fraction at the domain outlet. Negligible differences (relative deviation of 0.025%) have been observed when using the finer mesh.

Table 5.2.: The standard operating conditions used in the simulations: Inlet velocity, inlet temperature, operating pressure, inlet mole fractions of NH₃ and O₂, as well as the wire diameter and distance.

Description	Parameter	Value
Gas velocity at inlet	$u_{\rm in}$ / m s ⁻¹	0.75
Gas temperature at inlet	$T_{ m in}$ / K	423.15
Operating pressure	p / Pa	500000
NH_3 mole fraction at inlet	$x_{\rm NH_3}$	0.1
O_2 mole fraction at inlet	x_{O_2}	0.189
Wire diameter	$d_{ m w}$ / mm	0.1
Center-to-center wire distance	<i>D</i> / mm	$0.3 (3d_w)$

The boundary conditions are chosen according to the operating conditions of a typical mediumpressure plant: At the inlet of the domain, a constant velocity of $u_{in} = 0.75 \text{ m s}^{-1}$ is assumed. The inlet temperature is 423.15 K, the gas mixture at the inlet consists of 10 vol% of NH₃ in air and the operating pressure is 5 bar. These conditions are referred to as the *standard conditions* and will be used throughout this work, if not stated otherwise. A full description of the conditions is presented in Table 5.2. The chemical reactions and the respective heat of reaction are implemented as a boundary condition at the surface of the wire as described in Equations (3.14) and (3.15). The gas species source terms R_i are calculated via Equation (5.2) from the kinetic model outlined in the previous section. In cases, where thermal radiation effects are considered, an emissivity of $\epsilon_{Pt} = 1$ was assumed for the platinum wires.

To estimate if turbulence effects have to be accounted for, the Reynolds number Re of the flow is calculated according to Equation (3.31). The characteristic length L was chosen to be the wire diameter d_w and u is the free stream velocity, in this case the velocity at the inlet of the domain. Evaluating Re for conditions at the inlet of the domain ($u = 0.75 \text{ m s}^{-1}$), yields value of Re = 12.6. Re = 6.1 is obtained for conditions prevalent the outlet of the reactor ($u = 2.04 \text{ m s}^{-1}$, p = 5 bar, T = 1150 K), indicating that the flow in the reactor should be well described as laminar.

The model is set up and solved in ANSYS Fluent [41]. The mass fraction of N_2O at the outlet of the domain was chosen as the determining convergence criterion, since its balance equation turned out to show the slowest convergence behavior.

5.3. Two-dimensional study of reactive flow over a single wire

In the following section the results of the single wire CFD model are presented. The resulting flow-, temperature and concentration profiles will be discussed as well as the effect of inlet velocity, wire diameter, wire spacing and surface area on the formation of N_2O .

5.3.1. Profiles of flow, temperature and concentration around the wire

The computed velocity vectors around the wire are shown in Figure 5.2. The velocity profile was obtained from a simulation for the standard conditions of Table 5.2, but with an inlet velocity of 1.5 m s⁻¹.



Figure 5.2.: Velocity vectors around the catalytic wire obtained from a simulation with a velocity of 1.5 m s⁻¹ at the inlet. All vectors were normalized to the same length and colored according to their magnitude. For better visualization, only every second vector is shown.

A stagnation point at the front side of the wire can be observed, while at the rear a small symmetric re-circulation zone is occurring. Solving the model with an inlet velocity of 0.75 m s⁻¹, no re-circulation pattern was obtained behind the wire. This is in line with literature results of isothermal flow around a cylinder, where for Re > 5 two steady symmetric vortices are observed and only at Re < 46 a transition to an unsteady fluctuating flow occurs [128]. The calculations also agree with published results for flow around a heated cylinder, where data shows that the transition to a fluctuating unsteady flow pattern is shifted to higher Reynolds numbers, compared to the isothermal case [129, 130].



Figure 5.3.: Left: Computed streamlines and NH₃ mole fraction profile around the single wire. Right: The respective temperature profile.

The NH_3 concentration- and temperature profile around the wire from the simulation with an inlet velocity of 0.75 m s⁻¹ is shown in Figure 5.3. From the mole fraction profile, strong gradients can be observed, with very small NH_3 concentrations at the surface of the wires, which is expected for a mass transfer controlled reaction. These gradients are steeper at the front side of the wires compared to the rear. This implies, that the flux of ammonia to the catalyst surface is more pronounced at the stagnation point. Due to the strong exothermic net reactions, the catalyst wires heat up and the heat released is sufficient to maintain the reaction at high temperatures. The model predicts a wire temperature of

about 1130 K, which is in line with temperatures observed in industrial medium-pressure ammonia oxidation reactors [15, 21]. Due to the high thermal conductivity and the small diameter of the wire, the temperature is homogeneous throughout the wire. The strong gradients lead to transfer of heat from the hot wire to the initially cold surrounding gas, heating up the gas when passing the wire. Similar to the concentration profile, the temperature gradients around the stagnation point are steeper compared to the rear part of the wire, thus heat transfer rates are higher at the front.

These flow induced inequalities in local heat and mass transfer rates are also discussed in the context of industrial ammonia oxidation in [131]. How these variations in local ammonia transfer rate influence the kinetics and the selectivity to the by-products is a central topic of this work and will be discussed in greater detail in the subsequent chapters.

5.3.2. N₂O formation on a single wire

In the following, the product selectivity profiles around the catalyst wire are investigated. The differential selectivity of product species i at a surface element is given by the following formula:

$$S_i = \nu_i^{\rm N} \frac{R_i}{R_{\rm NH_3}} \tag{5.5}$$

where ν_i^{N} is the number of nitrogen atoms in a molecule of species *i*, R_i the net production of gas species *i* and R_{NH_3} the net consumption rate of NH₃. Since at conditions relevant for ammonia oxidation at medium pressures the kinetic model at hand predicts negligible N₂ formation, the discussion on selectivity is limited to the selectivity towards N₂O. These low nitrogen production rates were already observed by [94, 132], who investigated the present microkinetic model under similar conditions.

In Figure 5.4, the local N₂O selectivity is plotted against the perimeter of the wire for inlet velocities of 0.375 m s⁻¹, 0.75 m s⁻¹ and 1.5 m s⁻¹. An angle of 0 degrees corresponds to the tip of the wire while an angle of 180 degrees represents the rear of the wire. The N₂O selectivity S_{N_2O} shows a significant variation along the wire circumference, with the selectivity at the front being almost twice as high as at the back. This strong variation is observed for all three inlet velocities. In each case, N₂O formation is highest at the stagnation point at the front side and decreases constantly towards the rear side of the wire. In general, for higher flow velocities the model predicts an increase in local N₂O selectivity along the whole surface of the wire.

To reveal the origin of this effect, the surface reaction model under mass transfer limiting conditions is studied in greater detail. Besides improved accuracy, the advantage of multi-scale models combining detailed surface chemistry and flow induced transport is that they enable sensitivity analysis that reveal the role of individual elementary steps in the industrial process under real operating conditions.

In the following, such an analysis is carried out for the single wire case at standard conditions of Table 5.2. Therefore, in a first step, the species gas phase concentrations along the perimeter of the catalyst wire are calculated. They are shown on the left side of Figure 5.5. While the concentrations of O_2 and NO are almost constant along the circumference, the gas phase concentration of NH₃ exhibits a significant variation. In fact, the concentration of NO is lower at the front (5.26 mol m⁻³) and higher at the rear (5.35 mol m⁻³) while for the O_2 concentration the opposite is the case, i.e. 3.16 mol m⁻³ at the front and 3.06 mol m⁻³ at the rear. Due to the high thermal conductivity of platinum, the temperature gradients throughout the wire are negligible. Thus it can be concluded, that the observed variation of N_2O selectivity can be attributed to the varying profile of NH₃ concentration near the wire surface, which in turn is controlled by the intensity of local NH₃ mass transfer to the catalyst surface.

At this point it is noteworthy that, although the local selectivity is governed by the concentration profiles around the wire, the choice of the kinetics only has a minor influence on the near-surface



Figure 5.4.: Variation of the N₂O selectivity along the perimeter of the wire for inlet velocities of 0.375 m s⁻¹, 0.75 m s^{-1} and 1.5 m s^{-1} .

concentrations¹ of NO, O_2 and NH_3 . Under the assumption that the overall reaction is limited by external mass transfer of NH_3 , the gas concentrations are almost entirely controlled by the stoichiometry and the intensity of O_2 and NO mass transfer relative to the NH_3 mass transfer, so that details of the chosen mechanistic model have only little influence on the concentration profiles. A more detailed explanation for this will be given in chapter B of the appendix.



Figure 5.5.: Left: Gas phase concentrations of NH₃, O₂ and NO near the surface of the wire. The concentrations are plotted along the perimeter of the wire. The concentration of NH₃ is enlarged by a factor of 10² for better visualization. Right: Respective surface coverages along the perimeter of the wire. The coverages of NH₃, N and NO are scaled by factors of 10⁶, 10⁵ and 10² respectively for better visualization.

The coverages of the surface species are plotted against the perimeter of the wire in the graph on the right hand side of Figure 5.5. The surface coverage of oxygen (O-a) shows a minimum at the front and increases to a maximum on the back side of the wire. For the coverages of NO-a and N-a the opposite

¹Throughout this work the term *near-surface concentration* denotes the gas phase concentration at the interface between the solid catalyst and the gas phase.

trend is observed, where the maximum is found at the front side. The variation of N_2O selectivity can be explained with this distribution of surface coverages: According to the mechanism, the product selectivity is controlled by the relative rates of the reaction of a N-a species with O-a (to form NO-a), with NO-a (to form N_2O) and with another N-a (to form N_2). Both, the minimum oxygen coverage, as well as the maximum NO-a and N-a coverage favor a higher N_2O selectivity at the front side of the wire. At the rear the higher O-a coverage and the decreased coverages of NO-a and N-a contribute to higher NO selectivities.

From the selectivity and gas phase concentration profiles it has been concluded, that S_{N_2O} shows a positive dependence on the distribution of NH_3 concentration near the surface and that this dependence is essential to understand the variation of selectivity along the wire surface. To quantify this effect, it is useful to calculate the reaction orders [112] with respect to the gas phase concentrations near the catalyst surface:

$$n_{i,j} = \frac{c_j}{R_i} \frac{\partial R_i}{\partial c_j} = \frac{\partial \ln R_i}{\partial \ln c_j}$$
(5.6)

 $n_{i,j}$ is called the order of reaction R_i with respect to concentration of species j and yields the relative change in the production/consumption rate of species i, if the concentration of species j near the surface is changed, keeping all other concentrations fixed. In a similar manner the selectivity order of N₂O with respect to gas phase concentrations can be defined:

$$n_{S_{N_2O},j} = \frac{\partial \ln S_{N_2O}}{\partial \ln c_j}$$
(5.7)

where $n_{S_{N_2O},j}$ quantifies the normalized sensitivity of S_{N_2O} with respect to a change in concentration of species *j*. Based on the definition of the differential selectivity in Equation (5.5), it can be shown with little mathematical effort, that the selectivity order of N₂O is given by the difference of the orders of N₂O production and NH₃ consumption, both with respect to c_j :

$$n_{S_{N_2O},j} = n_{N_2O,j} - n_{NH_3,j}$$
 (5.8)

When evaluating the selectivity order of N₂O with respect to the concentration of ammonia for conditions at the front tip of the wire, a value of $n_{S_{N_2O},NH_3} = 0.68$ is obtained. The selectivity order is positive, thus S_{N_2O} increases with the NH₃ concentration near the surface, confirming the explanation of the preceding discussions. The selectivity orders with respect to the near-surface gas phase concentrations of the three relevant species NH₃, O₂ and NO (no other species appear as adsorbing species in the mechanism) are reported in Table 5.3.

Table 5.3.: First row: The selectivity orders of N₂O with respect to the gas phase concentrations of NH₃, O₂ and NO. The selectivity orders are evaluated for the conditions at the front tip of the wire. Second row: Normalized maximum variation of gas concentration around the wire. Third row: Product of selectivity order and normalized maximum variation of gas concentration which is an indicator of the impact of the concentration variation on the N₂O selectivity.

	NH_3	O_2	NO
$n_{S_{N_2O},j}$	0.680	-0.679	0.991
$\Delta c_j / c_{\max,j}$	0.618	0.033	0.019
$n_{S_{\mathrm{N_2O}},j}\cdot\Delta c_j/c_{\mathrm{max},j}$	0.420	-0.022	0.018

A value of $n_{S_{N_2O},O_2} = -0.68$ implies that the selectivity of N₂O declines with increasing O₂ concentration. Both, the concentration of ammonia and oxygen affect the selectivity to practically the same

degree, but work in different directions. With a value of $n_{S_{N_2O},NO} \approx 1$, the N₂O selectivity is nearly proportional to the gas phase concentration of NO.

Table 5.3 also provides the maximum normalized concentration difference $\Delta c_j/c_{\max,j}$ of the different species around the perimeter of the wire. The product $n_{S_{N_2O},j} \cdot \Delta c_j/c_{\max,j}$ represents a measure of the expected impact of the variation in the species' concentration along the wire on S_{N_2O} . As discussed previously, the variation of O₂ and NO concentration along the wire is small. As a consequence, these concentrations only have a minor influence on the observed N₂O selectivity profile, although their selectivity order is in the order of the one with respect to NH₃. Thus the data confirms the assumption that the selectivity of N₂O around the wire is nearly fully controlled by the distribution of near-wall ammonia concentration.

To understand the behavior of the reaction mechanism under mass transfer controlled conditions in greater detail and in order to elucidate, how an increased NH₃ near-surface concentration leads to higher N₂O formation, a degree of rate control analysis for the surface conditions met at the front tip of the wire in the simulation of Figure 5.3 is performed. The degree of rate control for each pair of forwardand backward reactions was computed according to Equation (4.13). A more detailed introduction and efficient strategies for the calculation of $X_{\text{RC},i}$ are presented in section 6.3. In short, the degree of rate control of step *i* was evaluated by simultaneously varying the rate constant of the forward- and backward reactions in the model which are treated as forward reactions only, $X_{\text{RC},i}$ was computed varying only the forward rate constant.

Table 5.4 lists the degree of rate control of ammonia consumption $X_{\rm RC,NH_3}$ for the different reactions evaluated at the front position of the wire. To analyze the existence of any partial equilibria, Table 5.4 also lists the ratio of forward and backward rates $r_{\rm f}/r_{\rm b}$ for each of the reversible reactions. From the results can be seen, that according to the kinetic model, the single rate determining step of ammonia oxidation under mass transfer controlled conditions is the adsorption of NH₃. All NH₃ molecules adsorbed on the surface are subsequently dehydrogenated to N and will later react to one of the products NO, N₂O or N₂.

Elementary step	$X_{\rm RC, NH_3}$	$r_{ m f}/r_{ m b}$	$r_{\rm net}$ / mol m ⁻² s ⁻¹
R1/R2	0.999	$3.217\cdot 10^3$	5.08
R3/R3	$8.728\cdot10^{-5}$	$1.101\cdot 10^4$	6.33
R5	$3.115\cdot10^{-4}$	_	5.08
R6/R7	$1.159 \cdot 10^{-9}$	1.001	4.99
R8	$2.644 \cdot 10^{-9}$	_	$1.51 \cdot 10^{-4}$
R9	$-3.186 \cdot 10^{-7}$	_	5.04
R10	$3.176 \cdot 10^{-7}$	_	0.05

Table 5.4.: D	Degree of rate control of ammonia consumption $X_{ m RC, NH_3}$, ratio c	of forward and backward rate $r_{ m f}/r_{ m b}$
а	and net rate $r_{ m net}$ of the elementary steps, all evaluated at the co	onditions met at the wire tip in the
S	simulation of Figure 5.3.	

Oxygen adsorption is not rate determining ($X_{\rm RC} = 0$) but at the same time is not in partial equilibrium ($r_{\rm f}/r_{\rm b} \gg 1$). The most abundant surface species on the a-sites is oxygen, so that the rate of oxygen adsorption is mainly controlled by its own coverage. A higher oxygen coverage leads to a lower rate of adsorption and vice versa. In steady state, the O coverage is adjusted such that the rate of oxygen adsorption is balanced by the rate of oxygen consumption for the NH₃ oxidation. In this way the oxygen coverage and the rate of oxygen adsorption is indirectly controlled by the rate of ammonia adsorption. The higher NH₃ concentrations at the front side of the wire are associated with higher rates of NH₃

adsorption and hence higher O consumption. This explains the lower oxygen coverage at the front side of the wires, despite the slightly higher gas phase O_2 concentration at this position.

NO adsorption is in partial equilibrium with the gas phase NO concentration ($r_{\rm f}/r_{\rm b} \approx 1$). The maximum in the NO coverage at the front side of the wire (despite a slightly higher NO gas phase concentration at the rear side) can be explained by the fact that NO is displaced by O atoms that bind more strongly to the surface than NO. In this way the observed maximum of the NO coverage at the front side of the wire is a direct consequence of the higher NH₃ concentration and hence lower O coverage in this position.

5.3.3. Effect of wire diameter and spacing on the N₂O selectivity

To get a first idea about the potential effect of the gauze geometry on the product selectivity, the wire diameter d_w and the center-to-center distance D were changed. For wire diameters of 50 µm and 100 µm, the wire distances of $2d_w$, $3d_w$ and $4d_w$ were studied. The resulting integral NH₃ conversion and N₂O selectivity are listed in Table 5.5. Since it is the sub-stoichiometric component in the feed, the integral selectivity of product species *i* is calculated with respect to NH₃ according to the following equation:

$$S_{i}^{\mathrm{I}} = \nu_{i}^{N} \frac{M_{\mathrm{NH}_{3}}}{M_{i}} \frac{\omega_{\mathrm{out},i} - \omega_{\mathrm{in},i}}{\omega_{\mathrm{in},\mathrm{NH}_{3}} - \omega_{\mathrm{out},\mathrm{NH}_{3}}}$$
(5.9)

Here ν_i^{N} is the number of nitrogen atoms in the molecule of species *i* and $w_{\text{in},i}$ and $w_{\text{out},i}$ the mass fractions at the inlet and the outlet of the reactor model. The integral conversion of NH₃ can be calculated from the following equation:

$$X_{\rm NH_3} = 1 - \frac{\omega_{\rm out, NH_3}}{\omega_{\rm in, NH_3}} \tag{5.10}$$

Table 5.5.: Integral NH3 conversion and N2O selectivity over a single wire for different combinations of wire
diameter d_w and center-to-center distance D.

$d_{ m w}$ = 50 $\mu m m$			$d_{ m w}$ = 100 $\mu{ m m}$		
D	$X_{\rm NH_3}$ / %	$S_{N_2O}^{I} / \%$	D	$X_{\rm NH_3}$ / %	$S_{\rm N_2O}^{\rm I}$ / %
$2d_{\rm w} = 100 \ \mu { m m}$	83.9	2.38	$2d_{\rm w} = 200 \ \mu { m m}$	62.5	1.81
$3d_{\rm w} = 150 \ \mu { m m}$	57.1	2.17	$3d_{\rm w} = 300 \ \mu { m m}$	36.7	1.58
$4d_{ m w}$ = 200 µm	40.7	2.04	$4d_{\rm w} = 400 \ \mu { m m}$	25.4	1.50

As expected, the conversion decreases with increasing wire distance. In case of the same absolute distance, the conversion around the wire with larger diameter is higher, due to a higher catalytic surface area and smaller surface-to-surface distance between the wires.

To investigate the effect on the product selectivity in greater detail, the local N₂O selectivity is plotted against the perimeter of the wire for the different combinations of d_w and D in Figure 5.6. In line with the previous results, a variation of N₂O selectivity along the wire circumference with a maximum selectivity at the front is observed in all cases. For a fixed wire diameter, an increased wire spacing leads to lower N₂O selectivities. Comparing the results for constant diameter-to-distance ratio, the wire with lower diameter favors N₂O production, even in the case where the wires are compared for the same absolute value of $D = 200 \,\mu$ m. In general, a more pronounced variation of selectivity along the wire surface is observed for smaller wire diameters d_w and shorter wire distances D.



Figure 5.6.: Variation of the N₂O selectivity along the perimeter of the wire for different wire distances. Left: Wire diameter of d_w = 50 µm. Right: Wire diameter of d_w = 100 µm. The wires were separated by $2d_w$, $3d_w$ and $4d_w$.

This trend can again be explained with the variations in NH₃ concentration due to NH₃ transport to the catalyst surface. A closer arrangement of the wires leads to a constriction, and thus acceleration of the flow between the wires. As a consequence, the rate of mass transfer to the surface increases and leads to higher NH₃ concentrations near the surface. As indicated by a selectivity order of $n_{S_{N_2O},NH_3} = 0.68$, the N₂O selectivity is positively correlated with the ammonia concentration, therefore an increased NH₃ concentration near the surface enhances N₂O formation. Due to larger diffusion lengths, the mass transfer resistance for a wire with a higher diameter is increased. Following the previous argumentation, this leads to lower near-surface concentrations of ammonia and thus explains the less pronounced N₂O production for larger wire diameters. An interesting configuration to discuss is the special case of equal total center-to-center distance: Despite the same value for *D*, for higher wire diameters the flow cross-section is narrower, leading to increased mass transfer. At the same time the diffusion lengths are increased. Concerning the N₂O selectivity, these two effects work in opposite directions, with the effect of mass transfer resistance to be prevailing as indicated by the higher selectivity for $d_w = 50 \,\mu\text{m}$ in Figure 5.6.

The observed increase in overall N_2O selectivity for larger wire diameters and for smaller wire distances is in line with the theoretical analysis by Warner. He investigated the impact of wire diameter and wire distance on S_{N_2O} , using an overall mass transfer coefficient obtained by a correlation for *Sh*. Of course, such an analysis in terms of overall mass transfer coefficients does not provide information on the variation of the local N_2O selectivity along the wire perimeter.

5.3.4. Effect of cauliflower formation on N₂O selectivity

During operation the catalyst undergoes structural changes leading to the formation cauliflower-shaped structures on the catalyst surface. These structures form in the first hours to days of a campaign and lead to an increase in the total catalytic surface area. To take this effect into account, a surface enhancement factor F_{Γ} has been introduced into Equation (5.2). TEM and BET measurements, as well as investigations using cyclic voltammetry suggest an increase in surface by a factor of about 10. This factor was chosen for F_{Γ} in the simulations. Industrial operators report that the NO selectivity improves during the first hours of operation after a new catalyst gauze has been installed. One possible explanation for this improvement in NO selectivity is related to the increase in catalytic surface area due to the structural changes. To investigate this effect of increased surface area, the surface enhancement factor in the model was varied. The results are shown in Table 5.6.

F_{Γ}	$X_{\rm NH_3}$ / %	$S_{ m N_2O}^{ m I}$ / %	$c_{ m NH_3}$ / mol m $^{-3}$	T / K
1	32.9	9.79	0.772	1081.5
2	34.9	5.18	0.407	1106.9
5	36.2	2.53	0.169	1123.9
10	36.6	1.58	0.085	1129.8

Table 5.6.: Integral NH3 conversion, integral N2O selectivity and NH3 concentration at the tip of the single wire,as well as wire temperature for different surface enhancement factors F_{Γ} .

The influence of an increased catalytic surface on the integral conversion is rather small. This is expected for an reaction that is limited by external mass transfer, as long as the hydrodynamic diameter of the wire does not change significantly. However, an enhanced surface area leads to decreased N₂O selectivity. Again this is explained by the the sensitivity of N₂O formation on the NH₃ concentration. Table 5.6 also lists the ammonia concentrations at the tip of the single wire for different surface enhancement factors. The increased internal wire surface causes a dilution of the near-surface concentration of NH₃. Reducing the ammonia concentration near the surface leads to a reduction in N₂O formation, as predicted by the sensitivity analysis presented in section 5.3.2. Thus, according to the results, the industrially observed decline in N_2O in the first hours of operation can, at least partly, be explained by the enlarged catalytic surface area due to cauliflower formation. The rather simple approach to describe the effect of an enhanced surface with a parameter like the surface enhancement factor F_{Γ} is based on the assumption, that due to the small length scale of the cauliflower structures, diffusion effects inside the structures can be neglected. Under this presumption, the gas phase concentration near the surface can approximated to be uniform. Based on computer tomography images of a restructured wire, Wiser performed CFD simulations explicitly capturing the cauliflower-shaped geometry [132] and compared the results to a wire with a smooth surface. The results of this study are briefly discussed in section 6.5.5.1.

5.3.5. Summary

In this section, NH_3 oxidation over a row of parallel catalyst wires in cross flow has been investigated using CFD simulations with a detailed surface kinetic model. In agreement with industrial practice, the model predicted mass and heat transfer limitations around the catalyst wires. The local N_2O selectivity is found to vary along the the perimeter of the wires, determined by the local concentration of NH_3 near the catalyst surface. An analysis with selectivity orders revealed a positive correlation between NH_3 concentration and N_2O selectivity. The local near-surface ammonia concentrations in turn are the result of different NH_3 mass flow rates caused by the local flow field around the wires. Due to a stagnation point of the flow at the front side of the wire, the N_2O selectivity is observed to have a maximum here, declining when moving towards the wire back side. Decreasing the wire spacing and the diameter of the wires increases the local mass transfer rates of NH_3 towards the surface and thus enhances N_2O selectivity. The effect of an increased surface area due to the growth of so cauliflower-shaped structures has been investigated. Increasing the wires surface area due to reconstruction of the catalyst leads to an dilution of ammonia concentration near the wall resulting in lower N_2O selectivities.

5.4. Two-dimensional study of reactive flow over a multi-wire configuration

First insight on the interaction of external flow and detailed surface reaction kinetics has been gained by studying a single wire in cross-flow. Now a step towards a slightly more realistic catalyst geometry is taken by adding additional rows of wires. The wires are arranged in ten parallel rows in staggered configuration as shown in Figure 5.7. The center-to-center distance between two cylinders within a row is 300 µm. Each row is shifted by 200 µm horizontally and 150 µm vertically relative to the previous layer (the main flow is in x-direction). Due to symmetry, only an axial section of half wires needs be considered, as denoted by the dashed box. The computational mesh consists of triangular cells in the fluid and prism shaped layers have been introduced near the wires to improve the resolution of expected gradients. The resulting computational domain is 0.15 mm in height, 2.5 mm in length and contains \approx 28000 elements. As in the case of the single wire model, refining the mesh yielded only negligible changes in N₂O mass fraction at the outlet of the domain.



Figure 5.7.: Catalyst geometry and computational mesh. Only the domain inside the dashed rectangle needs to be taken into account in the simulation. The mesh is displayed for the area around the first two wires.

5.4.1. Profiles of flow, temperature and concentration without radiation

The solution of the CFD model yields the velocity, temperature and concentration profiles throughout the domain. These are shown in Figure 5.8 for the case where radiation effects are neglected.

From the mole fraction profile, strong gradients can be observed, with very small NH_3 concentrations at the surface of the wires, which is expected for a mass transfer controlled reaction. These gradients are steeper at the front side of the wires compared to the rear. This implies, that the reactive flux to the catalyst surface is more pronounced at the stagnation points. Furthermore it is observed that

almost all ammonia is consumed already after the third wire. For a mass transfer limited reaction, the conversion is independent of the chosen micro kinetic model and only determined by the convectionand diffusion-transport of the gas species, and thus is a purely physical phenomenon.



Figure 5.8.: Streamlines, NH₃ mole fraction and temperature throughout the catalyst obtained from the CFD model of the multi-wire geometry.

Due to the strong exothermic net reactions, the catalyst wires heat up and the heat released is sufficient to maintain the reaction at high temperatures. The model predicts a temperature of about 1130 K for the first wire, which is in line with temperatures observed in industrial medium-pressure ammonia oxidation reactors [15, 21]. Due to the high thermal conductivity and the small diameter of the wire, the temperature is homogeneous throughout a specific wire. The strong temperature gradients around the wires lead to transfer of heat from the hot wires to the initially cold surrounding gas, which heats up when passing through the catalyst. As in the case of NH₃ mass transfer, the temperature gradients around the stagnation points of the wires are higher compared to the rear part.

Table 5.7.: Integral conversions, integral product selectivities and temperature at the outlet of the reactor

	mouer
Parameter	Value
$X_{\rm NH_3}$ / %	99.90
$S_{\rm NO}^{\rm I}$ / %	98.64
$S_{N_{2}O}^{I}$ / %	1.35
$S_{N_2}^{I^2} / \%$	0.01
$T_{\rm out}$ / K	1108.7

 $X_{\rm NH_3}$ and integral product selectivities at the reactor outlet are listed in Table 5.7. For the conditions in Table 5.2, the model predicts a selectivity of 1.35% towards N₂O, which agrees with values found in industrial applications. In contrast to industrial reactors, the results show no significant formation of N₂. This was already found by [94, 132], who investigated the present microkinetic model under comparable conditions.

The temperatures of the different catalyst wires are plotted in Figure 5.9. Leaving the case of radiation out of the discussion, the temperature is increased for the first wires of the gauze pack, asymptotically approaching a constant temperature at the outlet of the reactor. As conversion is almost at 100% after



Figure 5.9.: Wire temperatures as a function of axial position in the catalyst with (squared) and without (diamond) thermal radiation effects, adiabatic temperature (dotted line) and front wire temperature calculated according to Equation (5.17) (dashed-dotted line). The dashed lines indicate the temperature with the Lewis number increased and decreased by 10%, neglecting radiation effects.

the first wires, this constant temperature equals the adiabatic temperature (T_{ad}). The model predicts the temperature of the first wire to be roughly 20 K above the adiabatic temperature, despite being surrounded by the cold, partially non-reacted gas mixture. This phenomenon was already discussed by Warner [16], who related this temperature overshoot to the Lewis number (*Le*) of the mixture being below unity.

For better understanding and later discussions, a simple relation for the temperature of the first wire based on the Lewis number of the fluid is derived. The temperature of a wire is controlled by the balance of heat released due to chemical reaction and the heat removed by convective heat transfer. The rate of heat production is controlled by the mass transfer of NH₃ towards the surface of the wire. The balance equation in terms of mass and heat transfer coefficients reads:

$$\beta_{\mathrm{NH}_3} c_{\mathrm{film}} \left(x_{\mathrm{b,NH}_3} - x_{\mathrm{s,NH}_3} \right) \Delta_{\mathrm{R}} H = \alpha \left(T_{\mathrm{b}} - T_{\mathrm{s}} \right)$$
(5.11)

In this equation the l.h.s. term describes the heat release due to chemical reaction, with β_{NH_3} the ammonia mass transfer coefficient, c_{film} the molar density of the film, $x_{\text{b,NH}_3}$ the ammonia mole fraction in the bulk, $x_{\text{s,NH}_3}$ the ammonia mole fraction near the surface of the wire and $\Delta_{\text{R}}H$ the enthalpy of reaction R1. The convective heat removal is represented by the term on the r.h.s with α being the heat transfer coefficient, T_{b} and T_{s} the gas temperature in the bulk and the wire temperature (due to the high thermal conductivity of the platinum and the small wire diameter, the temperature throughout the wire is nearly uniform). Assuming that the reaction is fully mass transfer controlled, $c_{\text{s,NH}_3}$ becomes small compared to the bulk concentration and can thus be neglected. Furthermore, rearranging Equation (5.11) for the wire temperature and expressing the respective transfer coefficients in terms of Sherwood (*Sh*) and Nusselt (*Nu*) numbers, as well as introducing the Lewis (*Le*) number,

yields:

$$T_{\rm s} = T_{\rm b} + \Delta_{\rm R} H \frac{Sh}{Nu} \frac{D_{\rm NH_3}}{\lambda} c_{\rm film} x_{\rm b, NH_3} = T_{\rm b} + \frac{\Delta_R H}{\rho_{\rm film} c_p} c_{\rm film} x_{\rm b, NH_3} \frac{Sh}{Nu} Le^{-1}$$
(5.12)

with
$$Sh = \frac{\beta_{\rm NH_3} d_{\rm w}}{D_{\rm NH_3}}$$
, $Nu = \frac{\alpha d_{\rm w}}{\lambda}$ and $Le = \frac{Sc}{Pr} = \frac{\lambda}{\rho c_p D_{\rm NH_3}}$

with d_w being the wire diameter. The Nusselt number for a heated cylinder in cross-flow is a function of Reynolds (*Re*) and Prandtl number (*Pr*) and is generally expressed as:

$$Nu = f(Re)Pr^{1/3}$$
 with $Pr = \frac{\mu c_p}{\lambda}$ (5.13)

The analogy for heat and mass transfer [56] yields a similar expression for the Sherwood number with the Prandtl number being replaced by the Schmidt number (*Sc*):

$$Sh = f(Re)Sc^{1/3}$$
 with $Sc = \frac{\mu}{\rho D_{\rm NH_3}}$ (5.14)

Sh and Nu are typically proportional to Re^m , with m varying between 0.3 and 0.4 [42, 55]. If Equations (5.13) and (5.14) are combined, one obtains

$$\frac{Sh}{Nu} = \left(\frac{Sc}{Pr}\right)^{1/3} = Le^{1/3} \tag{5.15}$$

which inserted into Equation (5.12) yields the final expression for the wire temperature:

$$T_{\rm s} = T_{\rm b} + \frac{\Delta_{\rm R} H}{\rho_{\rm film} c_p} c_{\rm film} x_{\rm b, NH_3} L e^{-2/3} = T_{\rm b} + \frac{\Delta_{\rm R} H}{c_{p,\rm m}} x_{\rm b, NH_3} L e^{-2/3}$$
(5.16)

with $c_{p,m}$ being the molar heat capacity (at constant pressure). Expressed in terms of the adiabatic temperature rise ΔT_{ad} , Equation (5.16) becomes:

$$T_{\rm s} = T_{\rm b} + \Delta T_{\rm ad} \, L e^{-2/3}$$
 (5.17)

with

$$\Delta T_{\rm ad} = \frac{\Delta_{\rm R} H}{c_{p,\rm m}} x_{\rm b, \rm NH_3}$$

Equation (5.17) states, that the temperature of the first wire is controlled by the adiabatic temperature rise and the Lewis number. Le < 1 yields wire temperatures above the adiabatic temperature. For Le equal or greater than 1, temperatures equal to or below T_{ad} are obtained.

Since in the reactor model full conversion is obtained, the adiabatic temperature rise is given by the temperature difference at the inlet and the outlet of the reactor. This takes into account the temperature dependence of c_p and the enthalpy effect of side reactions. As the physical quantities defining Le depend on the temperature and composition of the gas, the Lewis number is evaluated at the film conditions in front of the first wire. The film conditions are given by the mean of the quantities in the bulk and at the wire surface:

$$T_{\rm film} = \frac{T_{\rm s} + T_{\rm b}}{2} \quad \text{and} \quad x_{\rm film,i} = \frac{x_{{\rm s},i} + x_{{\rm b},i}}{2}$$
 (5.18)

	Surface	Bulk	Film
<i>T</i> / K	1128.65	423.15	775.93
$x_{\rm NH_3}$	0.0026	0.1000	0.0513
x_{O_2}	0.0609	0.1890	0.1249
$x_{\rm H_2O}$	0.1285	0.0000	0.0642
x_{NO}	0.9765	0.0000	0.0488
x_{N_2O}	0.0010	0.0000	0.0005

Table 5.8.: Temperature and species mole fractions at the surface, in the bulk and in the film in front of the first
wire. The mole fraction of N_2 is given by the balance.

where $x_{s,i}$ and $x_{b,i}$ are the mole fractions of species *i* at the surface of the wire and in the bulk. The calculated conditions in the film as well as at the surface and in the bulk are summarized in Table 5.8. With the respective film conditions, Le = 0.943 is obtained.

It is evident from Figure 5.9, that Equation (5.17) overpredicts the temperature of the first wire. This is expected as for its derivation the wire was assumed to be completely surrounded by cold, non-reacted gas. However, in the CFD model significant conversions are obtained already at the first wire. Thus, the temperature predicted by the equation represents an upper limit, that is reached in the extreme case of differential conversion at the first wire. According to the equation, the above-adiabatic temperature is mainly controlled by the Lewis number of the mixture. Thus, additional simulations have been carried out, where Le was changed by \pm 10% in order to asses the robustness of the predicted temperature rise. Altering Le is achieved by changing the mixture diffusion coefficients by the respective factor, while leaving the thermal conductivity constant. The range of \pm 10% is a rough estimate for the combined uncertainty for the diffusion coefficients and thermal conductivities tabulated in the literature. The resulting wire temperatures are included in Figure 5.9. As expected, changing the Lewis number does not affect the adiabatic temperature, except for an hardly noticeable degree due to a slight shift in product selectivity. In line with the prediction, decreasing the Lewis number leads to an even steeper temperature profile for the first wires. For the upper limit, a Lewis number greater than 1 is obtained and the temperatures of the first wires drop below the adiabatic temperature as expected. Whether the temperature of the first wires will be below or above the adiabatic temperature, is determined by the Lewis number of the mixture. Furthermore, the wire temperatures are expected to range in between the limits depicted in Figure 5.9.

We have published work in which a similar model was set up in COMSOL Multiphysics[®] [133], obtaining results that are in agreement with the observations in this work [49]. Differences in the results are due to different models and literature data used for diffusion coefficients and thermal conductivities, leading to a lower Lewis number than the one found in the present work. This leads to a more pronounced temperature overshoot of the first wires and shows that different results for the wire temperature may be obtained when using other data for physical properties of the gas.

5.4.2. Effect of radiation on catalyst temperature

To investigate the impact of radiation energy losses on the catalyst temperature, the calculations were repeated, but this time taking into account radiation between the different wires and the ambience. The calculated temperature profile is also shown in Figure 5.9. Radiation losses lead to a decrease in temperature throughout the whole gauze pack, lowering the exit temperature by approximately 29 K. Although radiation energy is lost mainly through the front wires, the model still predicts a temperature overshoot in the front part of the catalyst, even though the temperature profile begins to flatten out

compared to the case neglecting radiation. This discussion will be continued and consolidated this in the next section.

For the model with radiation, an increase in N₂O selectivity from 1.35 to 1.57% is obtained. This rise in selectivity is merely caused by the temperature drop of the catalyst due to radiation energy losses and is in line with investigations from Warner [16] and also reported for industrial reactors. Handforth and Tilley have investigated the precious metal losses for catalyst gauzes with different Pt/Rh alloys as a function of temperature [23]. According to the data in the paper, for a woven gauze ($d_w = 0.076 \text{ mm}$) with 90% Pt and 10% Rh a drop in the temperature of the first wire from 1129 to 1100 K reduces precious metal losses by about 17%. Even though, based on the accuracy of the data, the losses are a rough estimate, these numbers show that, while the qualitative behavior of the model remains unchanged, radiation effects can be significant and may have to be included into truly quantitative simulations.

5.4.3. N₂O selectivity on multiple parallel wires

So far, the effect of radiation and Lewis number on the wire temperatures of the multi-wire configuration has been investigated. The local N_2O selectivity as a function of the wire perimeter is plotted in Figure 5.10a for the first 6 wires. Simulations were conducted for the standard conditions in Table 5.2, neglecting radiation effects. As for the single wire case, a variation of N_2O selectivity along the wire circumference is observed for all wires, with a maximum selectivity observed at the front, constantly declining towards a minimum when moving to the rear side of the wires. Furthermore, the N_2O selectivity is decreases towards the outlet of the reactor when comparing the selectivity along different wires. Both effects are in line with the previous observations and arguments, where lower NH_3 concentrations cause reduced relative N_2O formation rates.

An exception from this trend is found at the second wire, for which the highest selectivity is observed, higher even than the selectivity around the first wire. This can partly be credited to the increased temperature of the first wire as seen in section 5.4.1. It was previously pointed out, that the extent of this temperature overshoot depends on the accuracy of the physical properties. To suppress this temperature effect, the calculation was repeated but this time fixing the temperature of all wires to $T_{\rm s} = 1100$ K, which is close to the adiabatic temperature. The resulting selectivities are shown in Figure 5.10b. As expected, due to the lowered temperature the selectivity of all wires is shifted towards higher values, especially for the front wires. The overall trend however remains unchanged and the highest N₂O selectivity is still found at the stagnation point of the second wire, thus leading to the conclusion that this is not entirely caused by the temperature effect.

Again the local variations in N₂O selectivity are determined by the distribution of NH₃ concentrations near the surface. The NH₃ concentrations along the perimeter of the respective wires are plotted in Figure 5.5c for the standard model and in 5.5d for $T_s = 1100$ K. As observed for the single wire, the N₂O selectivity correlates well with the ammonia concentration close to the catalyst surface. A maximum in NH₃ concentration is found at the front side of the second wire. Following the previous argumentation, this is the consequence of an increased mass transfer rate at this point. The enhanced mass transfer is caused by a flow effect due to the arrangement of the cylinders: Passing the first row of wires, the fluid is channeled and accelerated towards the second wire, which is positioned right behind the gap of the first row of wires. As a result, the flow impinges the second wire with a higher velocity, increasing the mass transfer and N₂O selectivity at the frontal area of the second wire. This is in line with results presented in Figure 5.4, where higher inflow velocities caused the N₂O selectivity to rise. In contrast, the third wire is shadowed by the first wire, thus a significant drop in N₂O selectivity is observed here. In general, the N₂O selectivity decreases, the further downstream a wire is located. This effect is mainly caused by



Figure 5.10.: (a) N₂O selectivity (top) and NH₃ concentration near the surface (bottom) plotted along the perimeter of the different wires in the 10-wire model. Inlet velocity is 1.5 m s⁻¹, all other operating conditions are identical to the standard conditions of Table 5.2, radiation is neglected. (b) The same as (a), but this time the wire temperature is fixed to $T_s = 1100$ K.

the ratio of NH_3 and O_2 concentrations. As there is an oxygen abundance in the feed gas stream, in relative terms, the ammonia concentration declines faster (almost to zero in the rear part of the catalyst) than the concentration of oxygen. An exception from this trend is found for the second wire, where this stoichiometric concentration effect is outweighed by the enhanced mass transfer characteristics. We have published similar work, where, due to different data for diffusion coefficients and thermal conductivities, a smaller Lewis number was obtained for the gas. In case of a variable wire temperature, the model predicted even the third wire to exhibit a higher N_2O selectivity at the front than the first wire. This is a result of the even further increased temperature of the first wire, due to a smaller Lewis number, and the negative correlation between catalyst temperature and N_2O selectivity.

These effects and their explanation are a first example how the individual wires perturb the flow field and how this perturbed flow influences the N_2O selectivity around the other wires. Due to this interaction, the selectivity of the whole gauze becomes a function of the gauze structure itself. Although such an influence of the gauze geometry on the selectivity has been observed experimentally for much more complex commercial gauze structures, so far no mechanistic explanation has been given for the described effect. The influence of external mass transfer, as a function of flow field and catalyst geometry,

on the network of surface reactions and the product selectivities will be studied in greater detail in chapter 6. A sensitivity analysis to quantify the influence of the mass transport will be developed and combined with CFD simulations of more complex three-dimensional catalyst structures.

5.4.4. Effect of pressure on NH₃ concentration profiles

In the industrial practice, ammonia oxidation is carried out at pressures ranging from 1 bar to 16 bar. Typical operating conditions are compared in Table 3.1. While high-pressure reactors are operated at significantly increased total mass fluxes, the increase in inlet velocity is moderate. To keep the analysis simple, the effect of different pressures is compared for a constant flow velocity.

Warner has shown both N_2O and N_2 selectivity to increase with increasing pressure for different catalyst loadings, keeping all other parameters fixed [16]. Other literature also describes a decreasing NO yield with increasing pressure, but there is either a lack of information concerning the remaining operating conditions [15, 21] or the gauze loading is not kept constant [23] upon the change in pressure. The explanation usually is given by thermodynamics and Le Chatelier's principle, since due to an increase in volume in reaction R1, higher pressures lead to lower conversions and higher slip of NH_3 [6, 15]. The slipped NH_3 then reacts with NO to N_2 via reaction R8. This conclusion however is questioned by Warner, because for the the increase in volume for reaction R8 is even larger, thus an increase in pressure should even favor NO formation [16]. Before starting with the discussion, it is useful, to recall that density and concentration increase linearly with pressure, thermal conductivity and viscosity are pressure independent and diffusion coefficients are inversely proportional to the pressure. Thus, at constant flow velocity, the Reynolds number increases proportional to the pressure.



Figure 5.11.: NH₃ mole fractions profiles throughout the gauze pack for different operating pressures of 1 bar, 4 bar and 16 bar. The simulations were carried out neglecting radiation.

Figure 5.11 shows the NH_3 mole fraction profiles throughout the catalyst for operating pressures of 1 bar, 4 bar and 16 bar. The simulations are carried out without accounting for radiation. For the lowest pressure almost full conversion is reached already after the first wire, while at 16 bar 7 wires are needed to reach about the same conversion. This is in line with the industrial application, where for low pressure plants only 3-5 gauze layers are installed while up to 50 layers are used for high pressure applications (see Table 3.1). In the mass transfer controlled regime, the conversion becomes independent of the underlying chemical kinetics. Since it is a pure physical effect, it is no surprise that the model predicts

the dependence of conversion on the pressure correctly.

The conversion is controlled by $J_{\rm NH_3}$, the total flux of ammonia to the catalyst surface and can be expressed in terms of a mass transfer coefficient and the concentration difference between the bulk and the surface:

$$J_{\rm NH_3} = \beta_{\rm NH_3} \, c_{\rm film} (x_{\rm b, NH_3} - x_{\rm s, NH_3}) \tag{5.19}$$

Noting that the concentration at the surface is negligible compared to the NH₃ bulk concentration and expressing β_{NH_3} in terms of *Sh*, one obtains:

$$J_{\rm NH_3} = \frac{Sh \, D_{\rm NH_3}}{d_{\rm w}} c_{\rm film} \, x_{\rm b, NH_3}$$
(5.20)

The gas concentration scales linear with p while the diffusion coefficient is proportional to 1/p, thus their product must be independent of pressure. According to literature, Sh is proportional to Re^m with $0.3 \le m \le 0.4$ for a single cylinder and a bank of cylinders in low Re cross flow [42, 55]. Since Reitself is proportional to p and Sc does not depend on pressure, the overall ammonia flux is proportional to p^m . Thus, the NH₃ conversion per catalyst surface area only slightly increases with pressure. Since for a constant feed velocity the NH₃ load of reactor scales linear with pressure, the integral conversion over the catalyst length decreases proportional to p^{1-m} .

Because the effect of pressure on conversion is a phenomenon entirely controlled by mass transfer, the effect can be well captured by using mass transfer correlations as demonstrated by Warner [16]. Figure 5.12 shows the integral conversion throughout the gauze pack for different pressures. At 1 bar, a conversion of about 70% is reached at the first wire, while for the same conversion five wires are needed at 16 bar. Based on the prior considerations, at 16 bar between $16^{0.6} \approx 5$ and $16^{0.67} \approx 6$ times the number of wires should be required to yield the same conversion as for the operation at 1 bar, which agrees well with the predictions of the CFD model.



Figure 5.12.: Integral conversion at different wires along axial direction for operating pressures between 1 bar and 16 bar.

5.4.5. Effect of pressure on the catalyst temperature

The left graph in Figure 5.13 shows the wire temperature profile throughout the catalyst for 1 bar, 4 bar and 16 bar. All calculations were performed with and without taking into account radiation. First, the results neglecting radiation are discussed. In the absence of radiation, for all pressures almost the same adiabatic temperature is reached at the reactor outlet. In steady state, the heat released by chemical reaction must equal the heat that is removed from the domain by convection:

$$c_{\rm in,NH_3} \, u \, \Delta_{\rm R} H \, A = \rho \, u \, c_p (T_{\rm in} - T_{\rm ad}) A \tag{5.21}$$

where A is the cross sectional area of the reactor perpendicular to the flow direction, u the gas inlet velocity and $c_{\text{in,NH}_3}$ the ammonia concentration at the reactor inlet. Rearranging yields the adiabatic temperature:

$$T_{\rm ad} = T_{\rm in} + \frac{c_{\rm in,NH_3} \,\Delta_{\rm R} H}{\rho \, c_p} \tag{5.22}$$

Here a constant heat capacity is assumed and all NH₃ is being converted to NO, according to reaction (R1), thus $\Delta_{\rm R} H$ equals the enthalpy of reaction R1. From Equation (5.22) it can be seen, that the pressure dependency of the inlet concentration and the density cancel each other out. Thus the adiabatic temperature does not depend on the pressure which is also predicted by the model. To be precise, the full CFD simulations show very small differences in the outlet temperatures for different pressures. At elevated pressures a higher N₂O selectivity is obtained. Since, per mole of converted NH₃, the reaction of NH₃ to N₂O (R7) is more exothermic than the reaction to NO (R1), a higher pressure results in a slightly elevated adiabatic temperatures. However, due to the small differences in N₂O selectivity, this effect is not very pronounced.

In section 5.4.1 the temperature overshoot of the first wires was discussed, which was qualitatively explained by the balance of heat release controlled by the diffusion of reactants to the wire surface and heat removal by convective heat transfer. According to the model predictions, the above-adiabatic temperature rise is more pronounced at higher pressures, approaching the limit given by Equation (5.17). This limit is reached, when the wire is completely surrounded by cold, non-reacted gas, i.e. in case of very small conversion on the respective wire. It was also demonstrated earlier, that higher pressures lead to decreasing conversion per wire (see Figure 5.11 and 5.12). As a consequence, at elevated pressures the front wires are surrounded by cold gas to a greater extent, thus the temperature overshoot is more pronounced compared to lower operating pressures. Here the conversion at the first wires is significantly higher and the wires are surrounded by hot reacted gas to a much greater extent. As a result, the flux of reactants to the wire decreases, as does the heat flux away from the wire. This drives the wire temperature towards the adiabatic temperature, which is reached when the heat fluxes become negligible and the wires are fully surrounded by the reacted gas mixture.

At 1 bar however, the front wire temperature falls below the adiabatic temperature, although the Lewis number is still below unity. This seems to be in conflict with the previous argumentation, as for Le < 1 one would expect an elevated front wire temperature, even if the conversion per wire is high due to the low pressure. At this point it is noteworthy, that the extend of mass transfer limitation exhibited in the simulations depends on the speed of the elementary reactions in the kinetic model relative to the diffusion of reactants in the gas phase. Transition from complete kinetic control to the full control of external mass transfer is smooth and does not occur instantly. Although the extend to which the reaction is controlled by external mass transfer in the model is significant, the kinetic system is not fully in the mass transfer limited regime. When moving into the kinetically controlled regime, the predictions of Equation (5.17) become less accurate, as the assumption $c_{s,NH_3} = 0$ is not valid anymore. In fact, a

non-zero ammonia concentration near the surface will lead to an additional negative term on the r.h.s. of Equation (5.17) and may cause T_s to fall below T_{ad} , even for Le < 1.

To get an idea how the system behaves under complete mass transfer limitation, the simulations were repeated, but this time replacing the full microkinetic model by the simple global reaction (R1). The rate R of this reaction is assumed to be first order with respect to NH₃ concentration:

$$R = k c_{\rm NH_3} \tag{5.23}$$

The rate constant was set to $k = 10^3$ m s⁻¹ to ensure complete mass transfer limitation. The respective results are shown in the right graph of Figure 5.13. In case of full mass transfer control, front wire temperatures are slightly elevated and the temperature profiles somewhat steeper. At 1 bar, the temperature of the first wire lies above the adiabatic temperature, as expected due to the previous explanations. As all NH₃ is converted to NO, the effect of selectivity on the adiabatic temperature vanishes and the outlet temperature is exactly the same for all pressures.



Figure 5.13.: Wire temperature as a function of the axial position in the catalyst for different operating pressures with (dashed line) and without (solid line) thermal radiation effects considered in the model. Left: With the full microkinetic model. Right: With a fast first-order reaction with respect to NH₃ concentration. For the calculation of the front wire temperature via Equation (5.17) (dashed-dotted line), the adiabatic temperature rise predicted by the particular CFD model at standard conditions is used.

The difference in the temperatures predicted by the two models is small though, as the model with the full mechanism is still far in the mass transfer controlled regime.

One should keep in mind, that the discussions on the temperature overshoot are based on the chosen value of *Le*. While literature suggest a positive Lewis number and hence a positive overshoot, Lewis numbers slightly above unity are also within the range of the estimated uncertainty. Even though the model is not able to predict the exact shape of the temperature profile, its value lies in providing insight into the complex interaction of physical phenomena on a fundamental level.

The effect of radiation on the temperature profile of the wires was already discussed in section 5.4.2, where in case of radiation a lowered catalyst temperature throughout the whole gauze pack was observed. While the energy losses via radiation are independent of the operating pressure (only a function of temperature), the heat release due to chemical reaction scales linear with pressure and thus the lowering of the gauze temperature is inversely proportional to p. As a consequence, radial losses

become more significant at lower pressures, as can be seen in Figure 5.13, where for a pressure of 1 bar the outlet temperature drops by almost 90 K.

Interestingly, although the temperature of the first wire is above the adiabatic temperature for 16 bar, it is lower than that of the succeeding one. This effect occurs for both, the model with the full kinetic model, as well as in the case of an first order reaction. Thus this phenomenon does not depend on the extent of mass transfer limitation. The explanation for this is rather simple: Since at higher pressures conversion per wire is lower, even the second wire is surrounded by significant amounts of cold non-reacted gas and resulting in a temperature overshoot of almost at the same extend as for the first wire. In contrast to the second wire, the radiation energy losses of the first wire are significantly higher. As a consequence, the first wire is at a lower temperature as the subsequent wire.

5.4.6. Effect of pressure on selectivity

Table 5.9 lists the integral N₂O selectivites at the outlet of the reactor for 1 bar, 4 bar and 16 bar. For all three pressures the selectivity towards N₂O increases when radiation losses are present. As already pointed out in the previous chapter, this is a mere temperature effect and can be explained by the temperature drop due to radiation and the negative correlation of S_{N_2O} with the catalyst temperature.

Table 5.9.: Effect of pressure and radiation on the integral N₂O selectivity.

Pressure / bar	$S_{\rm N_2O}^{\rm I}$ / %	$S_{N_2O}^{I}$ / %
	(without radiation)	(with radiation)
1	0.56	0.85
4	1.19	1.42
16	2.57	2.75

When discussing the selectivities at different operating pressures, the situation gets mechanistically more complex, as the pressure affects not only the wire temperature but also the gas species partial pressures. Concerning the reaction network implemented in the model, the kinetics are influenced by three effects which in turn are caused by an increased pressure:

- 1. Increase in wire temperature.
- 2. Increased gas phase concentrations of O₂ and NO,
- 3. Increased NH₃ concentration near the surface of the catalyst due to enhanced mass transfer.

To investigate these effects in greater detail, a normalized sensitivity of S_{N_2O} with respect to pressure is defined:

$$SC_{S_{N_2O},p} = \frac{p}{S_{N_2O}} \frac{\partial S_{N_2O}}{\partial p} = \frac{\partial \ln S_{N_2O}}{\partial \ln p}$$
(5.24)

The N₂O selectivity is a function of T, c_{NH_3} , c_{O_2} and c_{NO} which in turn are all affected by the operating pressure. As a consequence, the normalized sensitivity in Equation (5.24) is related to these 4 quantities via the chain rule:

$$SC_{S_{N_2O},p} = \sum_i \frac{\partial \ln X_i}{\partial \ln p} \frac{\partial \ln S_{N_2O}}{\partial \ln X_i} = \sum_i SC_{S_{N_2O},p}^{X_i}$$
(5.25)
where **X** is a vector containing the physical quantities T, c_{NH_3} , c_{O_2} and c_{NO} and $SC_{S_{N_2O,p}}^{X_i}$ denotes the sensitivity of N₂O selectivity with respect to the physical quantity X_i due to a change in pressure p. It is easy to see, that the occurring normalized partial derivatives of N₂O selectivity with respect to gas phase concentration are just the selectivity orders $n_{S_{N_2O,j}}$ which have already been introduced in section 5.3.2. The advantage of the formulation in Equation (5.25) is that the sensitivity is split up into the contributions of the different effects, allowing to investigate, quantify and discuss these effects individually.

The normalized sensitivity is evaluated for the conditions at the tip of the first wire, obtained from the model at standard operating conditions with radiation. Starting with a converged solution of the model, the simulation was repeated with the operating pressure increased by 0.1% and the normalized partial derivative of X_i with respect to p calculated from a finite difference approximation:

$$\frac{\partial \ln X_i}{\partial \ln p} \approx \frac{p}{X_i} \frac{X_i' - X_i}{p' - p}$$
(5.26)

Here X'_i denotes the temperature and concentrations obtained from the simulation with the increased operating pressure p'. The normalized partial derivatives of N₂O with respect to X_i can be obtained directly from the kinetic model by the solution of Equation (5.3). Table 5.10 list the normalized partial derivatives and the sensitivity of the N₂O selectivity.

Table 5.10.: Sensitivity of N₂O selectivity with respect to pressure. The normalized partial derivatives of X_i with respect to p and S_{N_2O} with respect to X_i , with $\mathbf{X} = [T, c_{NH_3}, c_{O_2}, c_{NO}]$. The third row contains all the individual contributions in the sum of Equation (5.25). Here $S_{S_{N_2O},p,X_i}$ denotes $S_{S_{N_2O},p}$ due to the effect of X_i .

	T	$c_{\rm NH_3}$	c_{O_2}	$c_{\rm NO}$
$\partial \ln X_i / \partial \ln p$	0.0176	0.3999	0.9668	0.9814
$\partial \ln S_{\mathrm{N_2O}} / \partial \ln X_i$	-6.7683	0.6770	-0.6758	0.9893
$SC_{S_{N_2O},p,X_i}$	-0.1194	0.2707	-0.6533	0.9708

The discussion starts with the effect of temperature. With a value of 0.018 only a small relative increase in wire temperature with respect to pressure is obtained, which is mainly caused by the above-adiabatic temperature overshoot effect of the first wire. As already discussed in the previous section, this is a pure physical effect and may be reasonably predicted by the model. The dependence of S_{N_2O} on temperature however is negatively correlated and very pronounced with an decrease of 6.7% per 1% increase in temperature, resulting in $SC_{S_{N_2O},p,T} = -0.12$, thus an overall slightly decreasing S_{N_2O} with pressure due to the effect of temperature. The temperature dependency of the N₂O selectivity seems to be well established at least for temperatures where NO decomposition does not yet play a significant role. It can therefore be assumed, that the temperature contribution to the pressure dependence is qualitatively predicted by the model.

The gas phase concentrations of O_2 and NO near the surface scale almost linearly with pressure, as they are not controlled by mass transfer. Taking into account the selectivity orders of $n_{S_{N_2O},O_2} = -0.68$ and $n_{S_{N_2O},NO} = 0.99$, it can be seen, that with higher O_2 concentration the N₂O selectivity decreases, while an increase in NO concentration favors N₂O production. This results in a combined contribution of c_{O_2} and c_{NO} on the pressure dependence of N₂O selectivity of 0.31, since the positive selectivity order of NO prevails. As the effects of O_2 and NO gas phase concentration depend on many details of the reaction mechanism, other plausible mechanisms might predict a different behavior with respect to N₂O selectivity.

The discussion finishes with the effect of NH₃ concentration near the surface of the catalyst. Since in the mechanistic model ammonia has its own adsorption site, and the coverages of adsorbed ammonia (NH₃-b) are always negligible, the rate of ammonia conversion is first order with respect to c_{s,NH_3} . The rate is equal to the flux of ammonia to the catalyst surface, which is controlled by the mass transfer of NH₃ and described by Equation (5.20). As already discussed, the pressure dependence of the diffusion coefficient and the ammonia concentration in the bulk cancel, and thus the dependence of the ammonia flux on the pressure is determined by the pressure dependence of Sh. For a bank of cylinders in cross-flow, literature suggest Sh to be proportional to p^m with m ranging between 0.33 and 0.4. This is in good agreement with the value of $\partial \ln c_{\rm NH_3} / \partial \ln p = 0.4$ predicted by the model. With a selectivity order of $n_{S_{N_2O},NH_3} = 0.68$, which is equal to the selectivity order of O₂ but with opposite sign, a $SC_{S_{N_2O}, p, c_{NH_3}} = 0.27$ is obtained. Experimental studies and other surface kinetic models support this positive correlation, thus the model should describe this effect qualitatively. Summing up all the individual the contributions, yields an overall normalized sensitivity of $SC_{S_{N,O}}$, p = 0.47. Accounting for radiation losses, increasing the pressure by a factor of four, should roughly double the N₂O selectivity, which is well reflected by the integral selectivities in Table 5.9. Although the derivatives and sensitivities were evaluated for conditions at the tip of the first wire, the qualitative behavior of the dependencies remain throughout the catalyst.

Altogether, the analysis shows that in the current model a change in pressure influences the N_2O selectivity indirectly by affecting four physical quantities. The influence of increased temperature, as well as the effect of increased NH₃ concentration near the surface due to increased mass transfer work in the opposite direction and should be qualitatively described by the model. The effects of O_2 and NO gas phase concentration are expected to be less robustly predicted by the reaction mechanism. Since their contribution is in the same order as the contribution of the first two effects, in conclusion the prediction of an increase in N_2O selectivity with pressure can be regarded as not very robust.

Despite the uncertainty in the physico-chemical parameters, analyses like these are useful, as they show the possible reactor behavior as a function of physical parameters and hence provide a framework to suggest necessary laboratory experiments.

5.4.7. Summary

In this section, the investigation of industrial ammonia oxidation has been expanded to multiple rows of parallel oriented Pt cylinders in cross-flow. In this scenario, the highest N_2O selectivity is observed at the tip of the wire in the second row. Due to a channeling effect of the first row of wires, the fluid is accelerated towards the stagnation point of the wires in the second row, thus further enhancing mass transfer and N_2O selectivity. The third-row wires however are shadowed by the wires in the first row, thus showing significantly lower N_2O selectivity.

Taking into account radiation energy losses of the front wires, at 5 bar the adiabatic temperature at the reactor outlet drops by 29 K accompanied by a small rise in N₂O selectivity. Compared to the adiabatic temperature, the observed temperature of the front wires is raised, with the first wire being the hottest. This effect is controlled by the balance of heat release due to chemical reaction and heat removal from the wire by convective heat transfer and can be quantified using the Lewis number of the gas. A Lewis number lower than 1 results in a temperature overshoot, while for Le > 1 a sub-adiabatic wire temperature will be obtained. In the model presented in this work, the calculated Lewis number is slightly below 1 and depends on the accuracy of the chosen model and the quality of experimental data for diffusion coefficients and thermal conductivities. Thus for other models this temperature overshoot may be more pronounced or, on the other hand, a wire temperature below T_{ad} might be obtained.

Since the reaction is limited by external mass transfer, a larger number of wires is required at elevated

pressures in order to generate the same conversion. Thus the temperature overshoot is more pronounced at higher pressures, since conversion per wire decreases and the front wires are partially more surrounded by cold non-reacted gas. For higher pressures, the effect of radiation losses on catalyst temperature is less significant. Changing the pressure leads not only to a change in catalyst temperature but also affects the near-surface concentrations of NH_3 , O_2 and NO, which in turn all have an impact on the N_2O selectivity.

A sensitivity analysis revealed the pressure-induced effect of temperature and oxygen concentration to have a negative impact on N_2O formation, while the effect of ammonia and NO concentration favor N_2O selectivity. Supported by experimental findings, the predicted effect of temperature and NH_3 near-surface concentration can qualitatively be assessed as robust. In case of O_2 and NO gas phase concentrations, the predictions of the model need to be treated more carefully. Since the combined negative and positive contributions are in the same order, the overall model robustness regarding the pressure effect on product selectivity must be rated as weak.

5.5. Conclusion

Although industrial ammonia oxidation has for a long time been recognized as a mass transfer controlled process, and despite considerable research efforts invested in the understanding of the surface chemistry and the development of the corresponding kinetic models, to date the interaction between mass transfer and surface chemistry has been insufficiently discussed.

In this chapter two-dimensional simulations have been presented, that combine the computation of the flow-, temperature- and concentration profiles around the platinum catalyst wires with the solution of the chemistry on the wire surface.

The simulations have shown that current kinetic models are able to predict realistic N_2O selectivities under industrial operating conditions. Furthermore the model is able to resemble other essential features of the industrial process, such as mass and heat transfer limitation, catalyst temperature and adiabatic temperature rise.

It was furthermore demonstrated, that the selectivity of N_2O formation is controlled by the local interaction between flow field and surface chemistry. This leads to a local variation in the N_2O selectivity, with the selectivity being increased in areas of intensified gas-surface mass transfer. The interaction of local transport and surface chemistry leads to a number of effects observed in the simulations:

- 1. The N_2O selectivity is higher on the front side of a wire compared to the rear side. This is explained by the formation of a stagnation point on the front which leads to enhanced mass transfer.
- 2. Lower N₂O selectivity is observed where one wire is shadowed by another wire.
- 3. N₂O selectivity is generally highest on the front wires and decreases towards the rear wires.
- 4. Deviating from the general rule expressed in the previous point, in the parallel wire geometry, the point of highest N₂O formation is found on the front side of the second wire. This is explained by the flow-directing effect of the first row of wires that accelerates the flow towards a stagnation point on the second wire.
- 5. Increased flow velocity leads to increased N₂O formation.
- 6. Decreasing the wire distance leads to increased N_2O formation. This is explained by a smaller open cross-section leading to an acceleration of the flow and hence to increased mass transfer.

- 7. Increasing N_2O formation with decreasing wire diameter.
- 8. Increased active surface area of the wires due to the formation of cauliflower-shaped structures on the platinum surface leads to decreasing N₂O formation.

All the effects described above can be explained by an increased local mass transfer leading to increased formation of N_2O . Some of these effects that concern the local variation of the selectivity across the gauze surface have been observed for the first time the simulations (points 1, 2, 4 in the list above). Other effects were known before, either from considerations based on mass transfer coefficients (points 3, 5, 6, 7, 8) or because they have been observed in lab experiments or industrial practice (points 6, 7, 8).

Being aware of the uncertainty in the kinetic models, resulting from the fact that current reaction mechanisms have been developed from experiments at conditions far from industrial operating conditions, special emphasis is put on elucidating the features of the reaction mechanism that are responsible for the observed effect of local mass transfer on the product selectivity. The analysis shows that the effect is nearly completely controlled by $n_{S_{N_2O},C_{NH_3}}$, the sensitivity of N₂O selectivity towards the NH₃ near-surface concentration, in combination with the local distribution of the near-surface ammonia concentration. The distribution of the remaining reactants O₂ and NO plays only a minor role for the manifestation of the discussed phenomena, as their near-surface concentration is more or less unaffected by local mass transfer intensity an does not vary significantly along the different wires. As a consequence, independent of the mechanistic details, other reaction mechanisms that show a positive $n_{S_{N_2O},c_{NH_3}}$ will qualitatively reproduce the above listed findings. Future experimental and mechanistic work should therefore focus on a better measurement and understanding of $n_{S_{N_2O},c_{NH_2}}$.

It was shown, that the well-established global trends in the N₂O selectivity as a function of operating conditions and gauze parameters, as well as the local selectivity distributions observed, can be traced back to the positive selectivity order $n_{S_{N_2O},C_{MH_3}}$. From today's point of view, the positive sensitivity of N₂O formation towards an increased NH₃ concentration predicted by the reaction mechanism is not unrealistic. First, based on simple chemical reasoning, the assumption that higher NH₃ near-surface concentrations will lead to increased formation of side products has already been expressed in the early literature [74, 134]. Second, a number of other current reaction mechanisms have been investigated [10, 82, 90] and despite the differences in the details, they all predict a positive dependence of N₂O selectivity on the NH₃ gas phase concentration near the surface (not shown in this work). Finally, and most importantly, the assumption that higher NH₃ gas phase concentrations lead to increased side product formation is supported by the fact that the simulations predict a number of experimentally well-established trends, such as the effect of flow velocity and wire diameter on the selectivity. Since these global selectivity trends and the local selectivity variations are both based on the same feature of the mechanism, the experimental confirmation of the global selectivity trends at the same time increases the confidence in the other model predictions.

The fact that the gauze geometry has an effect on the selectivity has been observed in the industry for a long time, which led to the development of complex gauze designs. To the authors knowledge, the current study for the first time provides a mechanistic explanation for this observed influence of gauze geometry on selectivity. Furthermore, from the insights of this study, design principles for improved gauzes can be derived: An optimal gauze design should reduce the local mass transfer intensity on the wires.

Besides the effects controlling the N_2O selectivity, the model-based investigations have provided further insights on the effect of industrially relevant process parameters on the physical behavior of the reactor, most of these effects being independent from any details of the mechanistic model:

- 1. For a gas mixture with Le < 1 a temperature overshoot above the adiabatic temperature is obtained for the first wires of the gauze.
- 2. The temperature overshoot is more pronounced the lower the conversion per wire.
- 3. The NH₃ consumption rate per wire scales with approximately $p^{1/3}$. For a constant inlet velocity, the integral conversion over the whole catalyst is thus proportional to $p^{-1/3}$. This means that when doubling the operating pressure, about 1.6 times the catalyst equipment is required to maintain the same level of total conversion.
- 4. Although leading to the same adiabatic temperature in the rear part of the catalyst, an enhanced temperature overshoot for the first wires is obtained when increasing the operating pressure. This can be explained with an decrease in conversion per wire at elevated pressures.
- 5. N_2O selectivity is indirectly coupled with pressure via the influence of pressure on reactant concentrations and catalyst temperature.

The first point was already pointed out by Warner [16]. With the Lewis number of the gas being below unity, the model presented in this chapter predicts a temperature overshoot for the first wires. Due to the uncertainty in the thermal conductivity and diffusion coefficients, the absolute results have to be treated carefully. Here a more precise determination of the physical properties would help to increase the robustness of the model predictions. However, even with these uncertainties the model is still a useful tool for *what-if* scenarios and to achieve a better understanding of the effect that physical parameters have on the behavior of the reactor.

Points 1 and 3 from the list above may, at least in parts, explain the significant increase in precious metal losses observed in reactors operated at high pressures. If a plant operator was to detect an above adiabatic temperature for the first gauzes, one possible measure to reduce the temperature, and therefore the precious metal losses, would be to increase the Lewis number of the gas stream. This could be achieved for example by changing the composition of the feed stream, e.g adding water [16]. A lower temperature of the first wires however may come with an increase in N_2O selectivity, leaving the operators to weigh the different aspects under an economic point of view.

6. The influence of local mass transfer on surface kinetics and catalyst performance

6.1. Introduction

Besides the oxidation of ammonia in the course of the Ostwald process, there are other industrially relevant catalytic reactions that are controlled by mass transfer and where the product selectivity is potentially affected by the catalyst geometry. Further examples for this important class of reactions, generally conducted at high temperatures and short contact times, are the closely related HCN synthesis via the Andrussow- and the BMA process [135–137], the partial oxidation of methanol to formaldehyde over Ag catalyst [138, 139] and steam methane reforming [140]. Two example reactions, that have not yet been carried out on an industrial scale, but posing a promising alternative to the conventional process are the oxidative coupling of methane to form ethylene [141, 142] and the catalytic partial oxidation of methane for syngas production [136, 143]. For these type of reactions, there is only limited simulation work that provides coupled investigation of flow and surface chemistry over the catalyst. For example, [101, 102, 144, 145] have investigated the flow past catalytic wires, but none of these works studies the effect of the flow field around the wires on product selectivity.

In this chapter, the investigations concerning the effects of flow, geometry and mass transfer on the selectivity of the ammonia oxidation process will be continued, implementing a surface microkinetic model proposed by Traversac [90]. The parameters of this model are adjusted so that it yields integral product selectivities which lie in the typical range of industrial practice. A *degree of rate control* [109] analysis is performed with the two-dimensional CFD reactor model. This yields the response of the detailed reactor model to changes in the kinetic constants of the incorporated reaction kinetic model. By integration of mass transfer effects in terms of mass transfer coefficients into the reaction mechanism, a simplified version of this *reactor-scale* degree of rate control is presented. This so-called *degree of mass transfer control*, which was first introduced by Klingenberger [94], yields results close to those obtained from the full CFD model. Both approaches will be compared to a conventional degree of rate control analysis, where only the surface chemistry without external mass transfer is considered. It will be shown that only in case of incorporated transport effects realistic results for a sensitivity analysis of the reaction mechanism is obtained.

Subsequently, a new generalized procedure for rational geometric catalyst design is introduced, which allows to optimize the selectivity of arbitrary chemical processes that utilizes structured catalysts under mass transfer limiting conditions. In a first step, a degree of mass transfer control analysis is performed in order to obtain the sensitivity of product selectivity with respect to changes in mass transfer intensity. In a second step, reactor-scale flow simulations are carried out, without considering the full kinetic model, yielding the distribution of local mass transfer coefficients throughout the catalyst. The application of this procedure is then demonstrated using more complex three-dimensional catalyst geometries and a restructured catalyst wire with resolved microstructure.

The topic of the last section differs somewhat from the topics outlined above, as it deals with a general proof of the summation rule for the degree of rate control.

6.2. Kinetic model

In this section, a more detailed microkinetic model proposed by Traversac [90] is presented. This model is then extended with the description of species transport to the catalyst surface in terms of mass transfer coefficients.

6.2.1. Microkinetic model from Traversac

The investigations are continued, using a more detailed microkinetic model proposed by Traversac [90]. The mechanism is a collection of elementary reactions taken from different authors, which all were determined for a Pt(111) surface. This surface is believed to be the thermodynamically favorable modification of platinum at elevated temperatures and pressures prevalent in industrial ammonia oxidation. In contrast to the model developed by Kraehnert, the mechanism ensures thermodynamic consistency, which is considered to be important in kinetic studies [146, 147]. The mechanism consists of a total of 22 reversible reactions between eleven surface and seven gas species. Kinetic parameters are given in form of sticking coefficients S for all adsorption/desorption reactions and pre-exponential factors k_0 and activation energies E_a for all activated surface reactions. A full description of the elementary steps is presented in Table 6.1.

			• • • •	
Reaction	Equation	k_0 / s^{-1} , S (stick)	$E_{\rm a}$ / kJ mol $^{-1}$	b
R1	$NH_3 + Pt(s) \rightleftharpoons NH_3(s)$	$3.0 \cdot 10^{-2}$ (stick)	0	0
R2	$O_2 + 2 Pt(s) \rightleftharpoons 2 O(s)$	$3.0 \cdot 10^{-2}$ (stick)	0	0
R3	$H_2O + Pt(s) \rightleftharpoons H_2O(s)$	$7.0 \cdot 10^{-1}$ (stick)	0	0
R4	$H_2 + 2 Pt(s) \rightleftharpoons 2 H(s)$	$4.6 \cdot 10^{-2}$ (stick)	0	0
R5	$NH_3(s) + O(s) \rightleftharpoons NH_2(s) + OH(s)$	$1.2\cdot10^{12}$	42	0
R6	$NH_2(s) + O(s) \rightleftharpoons NH(s) + OH(s)$	$6.1\cdot10^{12}$	87	0
R7	$NH(s) + O(s) \rightleftharpoons N(s) + OH(s)$	$7.6 \cdot 10^{12}$	84	0
R8	$NH_3(s) + OH(s) \rightleftharpoons NH_2(s) + H_2O(s)$	$1.6\cdot 10^{11}$	73	0
R9	$NH_2(s) + OH(s) \rightleftharpoons NH(s) + H_2O(s)$	$3.4\cdot10^{12}$	22	0
R10	$NH(s) + OH(s) \rightleftharpoons N(s) + H_2O(s)$	$5.1\cdot10^{11}$	35	0
R11	$NH_3(s) + Pt(s) \rightleftharpoons NH_2(s)s + H(s)$	$5.6 \cdot 10^{11}$	93	0
R12	$NH_2(s) + Pt(s) \rightleftharpoons NH(s) + H(s)$	$5.0\cdot10^{12}$	110	0
R13	$NH(s) + Pt(s) \rightleftharpoons N(s) + H(s)$	$7.2 \cdot 10^{12}$	118	0
R14	$O(s) + H(s) \rightleftharpoons OH(s) + Pt(s)$	$1.0\cdot10^{11}$	$51 - 5\theta_{\rm O} - 14\theta_{\rm H}$	0
R15	$H_2O(s) + O(s) \rightleftharpoons 2 OH(s)$	$1.0\cdot10^{11}$	$53-90\theta_{O}$	0
R16	$OH(s) + H(s) \rightleftharpoons H_2O(s) + Pt(s)$	$1.0\cdot 10^{10}$	$52-52\theta_{O}-13\theta_{H}$	0
R17	$N(s) + O(s) \rightleftharpoons NO(s) + Pt(s)$	$1.0\cdot10^{13}$	121	0
R18	$NO + Pt(s) \rightleftharpoons NO(s)$	$9.0 \cdot 10^{-1}$ (stick)	0	0
R19	$N(s) + N(s) \Rightarrow N_2 + Pt(s)$	$1.0\cdot10^{11}$	79	0
R20	$NO(s) + N(s) \rightleftharpoons N_2O(s) + Pt(s)$	$1.0\cdot10^{10}$	93	0
R21	$N_2O(s) \rightleftharpoons N_2 + O(s)$	$2.0\cdot10^{14}$	155	-0.45
R22	$N_2O + Pt(s) \rightleftharpoons N_2O(s)$	$2.0 \cdot 10^{-3}$ (stick)	0	0

 Table 6.1.: Microkinetic model for ammonia oxidation on Pt(111) [90]. (s) indicates that a species is bound to the catalyst surface. Values for the dimensionless sticking coefficients are labeled with (stick). The activation energies of R14, R15 and R16 depend on the surface coverages of O(s) and H(s).

The rate constants for adsorption reaction j are calculated using collision theory and given by the

Hertz-Knudsen equation:

$$k_j = \frac{S_j}{\Gamma} \sqrt{\frac{\mathbf{R}T}{2\pi M}} \tag{6.1}$$

where S is a sticking coefficient. For the adsorption-/desorption steps, the unit of k_j is m³ mol⁻¹ s⁻¹. The rate constants of all surface reactions are calculated using the Arrhenius equation, where the pre-exponential factor k_0 is a fixed parameter:

$$k_j = k_{0,j} T^b \exp\left(-\frac{E_{\mathrm{a},j}}{\mathrm{R}T}\right)$$
(6.2)

Since every elementary step is formulated reversible, the net rate of an elementary reaction is given by the difference of the forward- and the reverse rate:

$$r_{j} = k_{j} \prod_{i} c_{i}^{|\nu_{ij}|} \prod_{i} \theta_{i}^{|\nu_{ij}|} - \frac{k_{j}}{K_{\text{eq},j}} \prod_{i} c_{i}^{|\overline{\nu}_{ij}|} \prod_{i} \theta_{i}^{|\overline{\nu}_{ij}|}$$
(6.3)

Here ν_{ij} is the stoichiometric coefficient of species *i* in the forward reaction of step *j*, while $\overline{\nu}_{ij}$ denotes the respective stoichiometric coefficient in the reverse reaction. Thermodynamic consistency of an individual step *j* is achieved by expressing the rate constant of the reverse reaction in terms of the forward rate constant and the chemical equilibrium constant $K_{eq,j}$. The equilibrium constant can be calculated from the standard-state Gibbs energy of the reaction:

$$K_{\rm eq} = \exp\left(-\frac{\Delta_{\rm R}G^0}{{\rm R}T}\right) \tag{6.4}$$

 $\Delta_{\rm R} G^0$ is given by the Gibbs-Helmholtz equation:

$$\Delta_{\rm R} G^0 = \Delta_{\rm R} H^0 - T \Delta_{\rm R} S^0 \tag{6.5}$$

 $\Delta_{\rm R} H^0$ and $\Delta_{\rm R} S^0$ are the standard-state enthalpy and entropy of reaction, which can be calculated from the enthalpies and entropies of formation of the individual chemical species involved:

$$\Delta_{\rm R} H^0 = \sum_i \Delta_{\rm f} H_i^0 \tag{6.6}$$

$$\Delta_{\rm R} S^0 = \sum_i \Delta_{\rm f} S_i^0 \tag{6.7}$$

The standard-state, denoted by the superscript index 0 , refers to a reference state with $p^{0} = 1$ bar. Since ideal gas behavior is assumed, the standard state Gibbs energy, enthalpy and entropy are independent of pressure and only a function of temperature. According to Kirchhoff's law, at constant pressure, the standard state enthalpy at a specific temperature T can be obtained by integration of the heat capacity c_{p} :

$$\Delta_{\rm f} H_i^0(T) = \int_{T_{\rm ref}}^T c_{p,i} \, \mathrm{d}T' + \Delta_{\rm f} H_i^0(T_{\rm ref}) \tag{6.8}$$

In a similar fashion the entropy of formation is calculated:

$$\Delta_{\rm f} S_i^0(T) = \int_{T_{\rm ref}}^T \frac{c_{p,i}}{T} \, \mathrm{d}T' + \Delta_{\rm f} S_i^0(T_{\rm ref}) \tag{6.9}$$

 $T_{\rm ref}$ is the reference temperature which is set to 298.15 K. The heat capacities are expressed in terms of temperature dependent polynomials. The polynomial coefficients for the gas species and the values for $\Delta_{\rm f} H_i^0(298.15 \text{ K})$ and $\Delta_{\rm f} S_i^0(298.15 \text{ K})$ are taken from [43] and listed in chapter A of the appendix. For the surface species, the respective heat capacities were obtained from [90], where c_p was calculated from models of statistical thermodynamics. The surface species molecules were assumed to have translational, vibrational and rotational degrees of freedom. The calculated thermodynamic data was fitted to the respective polynomials as a function of temperature. For a detailed description of the procedure and the respective polynomial coefficients for the surface species c_p , see [90].

The net rates of the individual species are given by the sum over all elementary reactions:

$$R_i = \Gamma F_{\Gamma} \sum_j \nu_{ij} r_j \tag{6.10}$$

Similar to the kinetic model developed by Kraehnert, a surface enlargement factor of $F_{\Gamma} = 10$ is used. The steady state surface coverages are obtained by integrating the system of ODEs in Equation 6.11 until steady state is reached, using the numerical solver IDAS from a MATLAB implementation of the SUNDIALS package [127].

$$\frac{\mathrm{d}\theta_i}{\mathrm{d}t} = \frac{R_i}{\Gamma} \tag{6.11}$$

The parameters in Table 6.1 are the values originally published by Traversac. Under industrial conditions, the selectivities predicted by the model are deviate from selectivities found in the industrial practice. To obtain more realistic predictions, the kinetic parameters of the model were adjusted. Details of the respective procedure are described in section 6.4.

6.2.2. Microkinetic model with external mass transfer

Due to the strongly mass transfer limited reaction, concentration gradients develop around the catalyst wires and the species concentrations near the catalyst surface deviate significantly from the gas concentrations in the bulk. Thus using bulk gas concentrations and neglecting mass transfer effects leads to erroneous predictions of the kinetic model. In order to investigate the kinetic model under realistic conditions without the need of a numerical expensive reactor model that resolves concentration gradients, mass transfer needs to be implemented into the respective kinetic mechanism. In the frame of the film model, the molar flux J of a gas species towards or from the catalyst surface can be expressed in terms of mass transfer coefficients:

$$J_i = \beta_i (c_{b,i} - c_{s,i})$$
(6.12)

where β_i is the mass transfer coefficient of species *i* which is given by the diffusion coefficient and the fictitious concentration boundary layer thickness Δx :

$$\beta_i = \frac{D_i}{\Delta x} \tag{6.13}$$

Assuming that Δx is the same for all gaseous species, the mass transfer coefficient of species *i* can be calculated from the mass transfer coefficient of ammonia and the ratio of respective diffusion coefficients:

$$\beta_i = \beta_{\rm NH_3} \frac{D_i}{D_{\rm NH_3}} \tag{6.14}$$

Under the assumption, that there is no accumulation of mass near the surface of the catalyst, the flux of a species must equal its consumption/production on the surface of the catalyst. The surface coverages and gas phase concentrations near the catalyst surface are given by the solution of the following system of coupled differential-algebraic equations (DAE):

$$J_i = \frac{R_i}{\Gamma} \tag{6.15}$$

$$\frac{\mathrm{d}\theta_i}{\mathrm{d}t} = \frac{R_i}{\Gamma} \tag{6.16}$$

The index *i* runs over all gas species in Equation (6.15) and over all surface species in Equation (6.16). It is emphasized, that the net rates *R* in Equations (6.15) and (6.16) are now a function of the species concentrations near the surface $c_{s,i}$ rather than the bulk concentrations $c_{b,i}$.

In steady state the rates of the surface coverages are equal to zero and the DAE system becomes a system of non-linear algebraic equations. To obtain the steady state state surface coverages the system of DAEs is integrated until steady state is reached, using the numerical solver IDAS from a MATLAB implementation of the SUNDIALS package [127].

6.3. Sensitivity analysis of detailed surface kinetic models

In this section, the concept of *degree of rate control* is presented in greater detail. This concept is then extended by incorporation of mass transfer into the analysis and the *degree of mass transfer control* is introduced. Two different approaches to calculate the degree of mass transfer control are presented.

6.3.1. Degree of rate control

The degree of rate control, defined in Equation (4.13), is a common and frequently applied tool for the investigation of microkinetic models in heterogeneous catalysis. It is used to identify significant elementary steps, such as rate-limiting or inhibition steps [116]. Since in industrial ammonia oxidation the reaction network leads to the parallel formation of main and side products, Equation (4.13) is rewritten to explicitly distinguish between the degree of rate control for the net rates R_j of the different species:

$$X_{\text{RC},i,j} = \frac{k_i}{R_j} \left(\frac{\partial R_j}{\partial k_i}\right)_{k_l \neq i, K_{\text{eq},i}}$$
(6.17)

where k_i is the *i*th component of vector k which contains the rate constants of all elementary steps:

$$\boldsymbol{k} = \begin{pmatrix} k_1 \\ k_2 \\ \vdots \\ k_{nR-1} \\ k_{nR} \end{pmatrix}$$
(6.18)

Here nR is the number of elementary reactions. The partial derivative in Equation (6.17) is evaluated, keeping the rate constants k_j of all other elementary steps $l \neq i$, as well as the equilibrium constant of step i ($K_{eq,i}$) fixed. The latter is achieved by varying the forward and the reverse rate constant of step i by the same factor. Equation (6.17) quantifies the relative change in the net rate of a species per relative change in the kinetic constant of elementary step *i*. In interests of clarity, from now on the rather bulky index in Equation (6.17) will be dropped, whenever writing out the partial derivative.

Summing over all elementary steps, $X_{\text{RC},ij}$ was found to be a conservative quantity that seems to obey the following summation rule [116, 122]:

$$\sum_{i} X_{\text{RC},i,j} = 1 \tag{6.19}$$

Although the conservation of $X_{\rm RC}$ is well known and broadly applied, a general validation of this summation rule has not been presented in the literature so far. In section 6.6 a prove of Equation (6.19) for an arbitrary surface kinetic model will be presented.

In many cases chemists and chemical engineers are more interested in selectivities rather than in absolute rates. To that end, analogous to Equation (6.17), the *degree of selectivity control* of elementary step i can be defined by simply replacing the net rates with the selectivity of product species P:

$$X_{\text{SC},i,P} = \frac{k_i}{S_P} \left(\frac{\partial S_P}{\partial k_i}\right)$$
(6.20)

With the definition of the differential selectivity in Equation (5.5), $X_{SC,i,P}$ can be written as the difference in the degree of rate control for the production of species *P* and the consumption of NH₃:

$$X_{\mathrm{SC},i,P} = X_{\mathrm{RC},i,P} - X_{\mathrm{RC},i,\mathrm{NH}_3}$$
(6.21)

As a consequence of the summation rule in Equation (6.19), summing $X_{SC,i,P}$ over all elementary steps must be equal to zero:

$$\sum_{i} X_{\mathrm{SC},i,P} = 0 \tag{6.22}$$

6.3.2. Degree of rate control with mass transfer

It seems obvious that in a mass transfer controlled process, the mass transfer of chemical species needs to be included in the degree of rate control analysis. Yet, besides the work of Klingenberger [94] and Foley [148], to the authors' knowledge, such type of sensitivity analysis including mass transfer effects has neither been described nor used in the literature. Applying the concept of degree of rate control to the microkinetic model with coupled mass transfer described in section 6.2.2 is rather straightforward. To explicitly distinguish such an analysis from the conventional degree of rate control where no mass transfer effects are considered, a small m in the superscript will be used:

$$X_{RC,i,j}^{m} = \frac{k_i}{R_j} \frac{\partial R_j}{\partial k_i}$$
(6.23)

In addition to the sensitivity with respect to the rate constants, the implementation of mass transfer allows to calculate the response of gas species net rates to changes in the mass transfer coefficient of the individual gas species. Therefore, the vector k in Equation (6.18) now contains the rate constants of all

elementary reactions, as well as the mass transfer coefficients of all gas species.

$$\boldsymbol{k} = \begin{pmatrix} k_1 \\ \vdots \\ k_{nR} \\ \beta_1 \\ \vdots \\ \beta_{nG} \end{pmatrix}$$
(6.24)

where nG is the number of gas species. Due to its importance and practical relevance, the sensitivity of the net rates with respect to changes in mass transfer coefficients will be called *degree of mass transfer control*. However, in the real practice it is not possible to change the mass transfer coefficient of each species individually. In most cases it is more convenient to consider the degree of mass transfer control with respect to the overall mass transfer. Mathematically speaking, this is equal to the sum over all contributions with respect to the individual mass transfer coefficients:

$$X_{\text{RC},\beta,j}^{m} = \sum_{i=nR+1}^{nR+nG} X_{\text{RC},i,j}^{m}$$
(6.25)

Notice that sum in Equation (6.25) only runs over all gas species. In the case of included mass transfer effects, a value of one is obtained when summing over all sensitivity coefficients:

$$\sum_{i} X_{\mathrm{RC},i,j}^{m} = 1 \tag{6.26}$$

Analogous to Equation (6.20), a degree of selectivity control for product species *P* can be defined:

$$X_{\mathrm{SC},i,P}^{m} = \frac{k_i}{S_P} \frac{\partial S_P}{\partial k_i} = X_{\mathrm{RC},i,P}^{m} - X_{\mathrm{RC},i,\mathrm{NH}_3}^{m}$$
(6.27)

6.3.3. Determination of partial derivatives

The calculation of the partial derivatives in Equation (6.23) poses the computational most expensive step in computing the degree of rate control. Two strategies for determining the full degree of rate control of kinetic models including mass transfer are illustrated. Both methods can be applied to a conventional degree of rate control analysis without mass transfer in the same manner.

6.3.3.1. Numerical evaluation

The straightforward approach to calculate the degree of rate control, that is used by many researchers, proceeds by approximating Equation (6.23) with a finite difference expression:

$$X_{\text{RC},i,j}^{m} = \frac{k_i}{R_j} \frac{\partial R_j}{\partial k_i} \approx \frac{k_i}{R_j} \frac{R'_j - R_j}{hk_i - k_i}$$
(6.28)

All parameters, i.e. rate constants and mass transfer coefficients, are successively increased by a small factor h. For every perturbed parameter, the respective steady state rates R'_j are obtained by numerically solving Equations (6.15) and (6.16). For a full degree of rate control analysis, this requires solving the system of DAEs nG + nR + 1 times, i.e. once to obtain the reference rates R_j and once for every perturbed rate constant and mass transfer coefficient.

6.3.3.2. Analytic evaluation using Jacobians

The second approach to calculate the degree of rate control, to which will be referred to as the *analytic* evaluation, is based on the fact that the vector \mathbf{R} , containing the steady state rates of all gas species, is a function of the parameter vector \mathbf{k} and the vector of surface coverages $\boldsymbol{\theta}$, which in turn also depends on the parameter vector. Temperature and bulk gas phase concentrations are kept fixed. Thus, the matrix containing the derivatives of all net rates \mathbf{R} with respect to all parameters \mathbf{k} can be expressed using the multivariate chain rule.

$$\frac{\partial \boldsymbol{R}}{\partial \boldsymbol{k}} = \boldsymbol{J}_{\boldsymbol{R},\boldsymbol{k}} + \boldsymbol{J}_{\boldsymbol{R},\boldsymbol{\theta}} \, \boldsymbol{J}_{\boldsymbol{\theta},\boldsymbol{k}} \tag{6.29}$$

In this equation $J_{R,k}$ denotes the Jacobian of the gas species rates R with respect to all parameters k. $J_{R,\theta}$ is the Jacobian of the gas species rates R with respect to all surface coverages θ and $J_{\theta,k}$ the Jacobian of surface coverages θ with respect to all parameters k. Notice, that the l.h.s. of Equation (6.29) is just the matrix notation of all partial derivatives in Equation (6.23).

$$\boldsymbol{J}_{\boldsymbol{R},\boldsymbol{k}} = \begin{pmatrix} \frac{\partial R_1}{\partial k_1} & \cdots & \frac{\partial R_1}{\partial k_{nR+nG}} \\ \vdots & \ddots & \vdots \\ \frac{\partial R_{nG}}{\partial k_1} & \cdots & \frac{\partial R_{nG}}{\partial k_{nR+nG}} \end{pmatrix}$$
(6.30)

$$\boldsymbol{J}_{\boldsymbol{R},\boldsymbol{\theta}} = \begin{pmatrix} \frac{\partial R_1}{\partial \theta_1} & \cdots & \frac{\partial R_1}{\partial \theta_{nS}} \\ \vdots & \ddots & \vdots \\ \frac{\partial R_{nG}}{\partial \theta_1} & \cdots & \frac{\partial R_{nG}}{\partial \theta_{nS}} \end{pmatrix}$$
(6.31)

$$\boldsymbol{J}_{\boldsymbol{\theta},\boldsymbol{k}} = \begin{pmatrix} \frac{\partial \theta_1}{\partial k_1} & \cdots & \frac{\partial \theta_1}{\partial k_{nR+nG}} \\ \vdots & \ddots & \vdots \\ \frac{\partial \theta_{nS}}{\partial k_1} & \cdots & \frac{\partial \theta_{nS}}{\partial k_{nR+nG}} \end{pmatrix}$$
(6.32)

Here nS is the number of surface species. At this point it should be mentioned, that although the net rates R also depend on the gas concentrations near the surface c_s , their respective Jacobian does not appear in Equation (6.29). Combining and rearranging Equations (6.15) and (6.12), one obtains an analytic expression for c_s as a function of k and θ . As a consequence, the response of R due to changes in the near-surface concentrations is implicitly contained in $J_{R,\theta}$ and $J_{\theta,k}$.

Once a converged solution is obtained, $J_{R,k}$ and $J_{R,\theta}$ can be calculated with little effort either directly from analytic expressions for the partial derivatives or using numerical difference schemes. The evaluation of $J_{\theta,k}$, however, is not a straightforward task, as in most cases there is no analytic relationship between θ and k. Of course, the most direct approach would be to again approximate the partial derivatives of the Jacobian using finite differences of the solutions of Equation (6.15) and 6.16. From a numerical point of view, this would not be significantly different from the method described in the previous section, as it requires a full solution of the DAE system for every parameter k_j . Similar to the gas species net rates, the rates of all surface species $\dot{\theta}$ also depend on the vectors k and θ . Once steady state is reached, the surface coverages are constant and $\dot{\theta} = 0$. Thus, for a small change of the surface species rates $d\dot{\theta}$ it can be written:

$$\mathrm{d}\dot{\boldsymbol{\theta}} = \boldsymbol{J}_{\dot{\boldsymbol{\theta}},\boldsymbol{k}} \,\mathrm{d}\boldsymbol{k} + \boldsymbol{J}_{\dot{\boldsymbol{\theta}},\boldsymbol{\theta}} \,\mathrm{d}\boldsymbol{\theta} = 0 \tag{6.33}$$

In this equation, $J_{\dot{\theta},k}$ is the Jacobian of the surface species rates $\dot{\theta}$ with respect to all parameters k and $J_{\dot{\theta},\theta}$ the Jacobian of the surface species rates $\dot{\theta}$ with respect to all surface coverages θ .

$$J_{\dot{\theta},k} = \begin{pmatrix} \frac{\partial \theta_1}{\partial k_1} & \cdots & \frac{\partial \theta_1}{\partial k_{nR+nG}} \\ \vdots & \ddots & \vdots \\ \frac{\partial \dot{\theta}_{nS}}{\partial k_1} & \cdots & \frac{\partial \dot{\theta}_{nS}}{\partial k_{nR+nG}} \end{pmatrix}$$
(6.34)
$$J_{\dot{\theta},\theta} = \begin{pmatrix} \frac{\partial \dot{\theta}_1}{\partial \theta_1} & \cdots & \frac{\partial \dot{\theta}_1}{\partial \theta_{nS}} \\ \vdots & \ddots & \vdots \\ \frac{\partial \dot{\theta}_{nS}}{\partial \theta_1} & \cdots & \frac{\partial \dot{\theta}_{nS}}{\partial \theta_{nS}} \end{pmatrix}$$
(6.35)

Rearranging Equation (6.33), one ends up with an algebraic equation for $J_{\theta,k}$:

$$J_{\theta,k} = -J_{\dot{\theta},k} \left(J_{\dot{\theta},\theta} \right)^{-1}$$
(6.36)

This equation quantifies the change of stationary surface coverages as a result of a differential change in the parameters. It is structurally similar to the analytic expression for the stationary sensitivity coefficients for species concentrations with respect to any parameter of a chemical kinetic system reported by Turányi et al. [108]. Inserting Equation (6.36) into Equation (6.30) yields the final expression for all the partial derivatives required for a full degree of rate control analysis:

$$\frac{\partial \boldsymbol{R}}{\partial \boldsymbol{k}} = \boldsymbol{J}_{\boldsymbol{R},\boldsymbol{k}} - \boldsymbol{J}_{\boldsymbol{R},\boldsymbol{\theta}} \, \boldsymbol{J}_{\dot{\boldsymbol{\theta}},\boldsymbol{k}} \, \left(\boldsymbol{J}_{\dot{\boldsymbol{\theta}},\boldsymbol{\theta}}\right)^{-1} \tag{6.37}$$

All Jacobians in Equation (6.37) can easily be obtained directly from the rate equations, provided a converged solution of the DAE system is present. The remaining task lies in calculating the inverse of $J_{\dot{\theta},\theta}$, which should computationally be significantly cheaper than repeatedly solving Equations (6.15) and (6.16) numerically. However, a few words should be given on the details of the matrix inversion: One feature that microkinetic surface reaction mechanisms have in common, is that the number of surface sites per unit area of catalyst is fixed. This means that the sum over all species surface coverages θ is equal to one. For kinetic models with more than one type of surface site (e.g Kraehnert's model) the sum over all coverages belonging to a specific type of surface site must equal one. As a consequence, the sum over all surface species rates $\dot{\theta}$ equals zero. This is still true if one takes the derivatives of $\dot{\theta}$ with respect to whatever variable, the sum remains zero. For $J_{\dot{\theta},\theta}$ this has significant consequences as its rows are not linearly independent and the matrix is singular. Thus the matrix of the form given in Equation (6.35) is not directly invertible. The procedure to circumvent this problem and to solve Equation (6.36) is presented in chapter C of the appendix.

To the author's knowledge, such a method for calculating the degree of rate control for a surface kinetic model has not yet been reported in the literature. The performance gained from this analytic evaluation is compared to the "classic" numerical evaluation via Equation (6.28) in section 6.5.2. There are further efficient numerical methods that can be applied to determine $J_{\theta,k}$ such as for instance the *Green function method* or automatic differentiation (AD) techniques, which are not in the focus of this work. Interested readers are referred to [107].

6.4. Tuning of the microkinetic model

This section describes the procedure of adjusting the parameters of the kinetic model proposed by Traversac. In order to obtain more realistic results, such an optimization needs to be done using an

appropriate reactor model. Therefore, the surface chemistry mechanism is implemented into the CFD model of the 10-wire configuration described in the previous chapter. The activation energies of a few selected elementary steps are then modified such that the CFD model with standard conditions of Table 5.2 yields selectivities of a typical medium-pressure ammonia burner. The respective target selectivities for the adjusted model are listed in Table 6.2.

Species	Selectivity / %
NO	96.0
N_2O	1.6
N_2	2.4

Table 6.2.: Product species target selectivities for the adjustment of the kinetic parameters.

6.4.1. Results with the original kinetic model and parameter identification

The ammonia- and product species mass fractions, as well as the temperature profiles obtained from the 10-wire CFD model with the original mechanism is shown in Figure 6.1. The values in the squared brackets denote the minimum and maximum values of the contour plots, going from dark blue (low values) to dark red (high values).

 NH_3 consumption is almost complete after the third wire. Strong mass fraction gradients around the wires indicate a mass transfer limitation which is in line with industrial observations and with the CFD-results obtained using the kinetic model from Kraehnert, which were discussed in section 5.4.1. The model also predicts the variation of the boundary layer thickness around the wire circumference. Thus, also for this kinetic model, an increased NH_3 mass transfer rate at the stagnation point at the front side of the wires can be observed. This is rather unsurprising, as for a mass transfer controlled reaction, the shape of the boundary layer is controlled by the flow field around the wires and independent of the details of the mechanistic model. Similar to the concentration profiles, strong temperature gradients are observed, leading to heat transfer from the hot wires to the colder surrounding gas.

Besides NO formation, the model forecasts the production of significant amounts of N_2O and N_2 . While the formed nitric oxide and nitrogen are stable, N_2O is slightly decomposed in the rear part of the catalyst. The latter is in contradiction to experimental results from Warner [16], who added additional layers of catalyst gauzes and observed neither a significant decrease in NO- nor in N_2O selectivity. In addition, also Traversac did not measure any significant NO and N_2O decomposition in presence of oxygen at temperatures around 800 °C [90]. The production of hydrogen is not predicted by the model which is in agreement with experimental results and other kinetic models, and thus will be excluded from all discussions following.

Table 6.3.: Integral NH ₃ conversion, integral product selectivities and temperature at the outlet of the reaction	зr
model obtained for the original parameters of the microkinetic model.	

Parameter	Value
$X_{\rm NH_3}$ / %	99.83
$S_{ m NO}$ / %	93.85
$S_{ m N_2O}$ / %	3.69
S_{N_2} / %	2.46
$\tilde{T_{\mathrm{out}}}$ / K	1118.1

Table 6.3 lists the integral selectivities and the gas temperature at the outlet of the reactor. With a selectivity of 3.69%, N₂O formation is significantly increased compared to industrial results, while the predicted NO selectivity of 93.85% is comparably low.

Based on this observations, the general steps for the optimization procedure of the mechanistic model are as follows:

- 1. Identify elementary steps which control the net reaction rates and selectivities of the product species.
- 2. Suppress N₂O decomposition.
- 3. Adjust the activation energies of the identified elementary steps such that the CFD model yields the target selectivities in table 6.2.

In order to determine the sensitivities of the species selectivities with respect to changes in the activation energy of an elementary step, a degree of selectivity control analysis of the microkinetic model with mass transfer is carried out. The analysis is evaluated for the conditions at the tip of the first wire of the CFD model. The sensitivities of N₂O and N₂ selectivity are shown in Figure 6.2. For the sake of clarity, the results are shown only for a selection of elementary steps. The X_{SC}^m of all steps not displayed is insignificant.



Figure 6.1.: NH₃- and product species mass fraction fields as well as temperature field from the CFD calculation with the original kinetic model.

The results reveal that, besides the adsorption/desorption of NH_3 and O_2 (R1 and R2) the product selectivity is mostly controlled by R17 (formation of NO(s)), R19 (formation of N_2) and R20 (formation of $N_2O(s)$). It seems reasonable that while an increase in the rate of R17 supresses the selectivity of both side products, R19 strongly favors N_2 selectivity and R20 the selectivity towards N_2O . Therefore, the activation energy of these three elementary steps are identified as sensitive parameters for the optimization procedure. The parameters of R1 and R2 are not considered, since the adsorption steps are modeled using collision theory and therefore regarded as fairly robust. Even small uncertainties in the activation energies of surface reaction steps have an comparably strong impact on the elementary rates and thus are better suited for an optimization. The mass transfer coefficient is of course not a reasonable parameter to tune, as it is obviously not related to the surface chemistry and determined by the flow and the catalyst geometry.



Figure 6.2.: Degree of selectivity control for N₂O and N₂ obtained for the original kinetic model with mass transfer. The sensitivities are evaluated for conditions prevalent at the tip of the first wire of the CFD model.

6.4.2. One-dimensional pseudo-homogeneous PFR model

Because an automatized approach is applied for the parameter optimization, the usage of the full CFD model seems unfavorable, due to the high numerical effort. Therefore, the full reactor model is replaced by a simplified, one-dimensional isothermal pseudo-homogeneous plug-flow reactor (PFR). This approach was already successfully used by Klingenberger [94]. The gas species bulk concentrations are given by the following system of ODEs:

$$\frac{\mathrm{d}c_{\mathrm{b},i}}{\mathrm{d}x} = \frac{a_{\mathrm{s}}}{u(x)}R_i \tag{6.38}$$

The steady state net rates R_i are given by the solution of the full microkinetic model with mass transfer according to Equations (6.15) and (6.16). The velocity u(x) depends on the position in the reactor and a_s is the surface-to-volume ratio of the catalyst.

For the solution of Equation (6.38), a reasonable choice for the catalyst temperature and the mass transfer coefficient of ammonia β_{NH_3} has to be made. From the solution of the full CFD model, a conversion weighted temperature \overline{T}_X and mass transfer coefficient $\overline{\beta}_{\text{NH}_3,X}$ can be calculated:

$$\overline{T}_{X} = \sum_{i} \frac{T_{i} \left(1 - X_{\text{NH}_{3},i}\right)}{\sum_{j} 1 - X_{\text{NH}_{3},j}}$$
(6.39)



Figure 6.3.: NH₃-, NO- and N₂O mole fraction along the axial coordinate of the reactor predicted by the 10-wire CFD model (solid line) and the one-dimensional pseudo-homogeneous PFR model (dashed line). For the calculations the kinetic model with original parameters was used.

Here T_i is the temperature of wire *i* and $X_{NH_3,i}$ the integral ammonia conversion directly behind the respective wire.

$$\overline{\beta}_{\text{NH}_{3},X} = \sum_{i} \frac{\beta_{\text{NH}_{3},i} \left(1 - X_{\text{NH}_{3},i}\right)}{\sum_{j} 1 - X_{\text{NH}_{3},j}}$$
(6.40)

The average mass transfer coefficient of the *i*th wire is calculated as an integral average of the local mass transfer coefficients weighted with the local rate of ammonia consumption along the surface of the wire:

$$\overline{\beta}_{\mathrm{NH}_3} = \frac{\int\limits_{A}^{A} \beta_{\mathrm{NH}_3} J_{\mathrm{NH}_3} \,\mathrm{d}A}{\int\limits_{A}^{A} J_{\mathrm{NH}_3} \,\mathrm{d}A} \tag{6.41}$$

The local mass transfer coefficient can be calculated from the the local flux of ammonia to the catalyst surface:

$$\beta_{\rm NH_3} = \frac{J_{\rm NH_3}}{c_{\rm b, NH_3} - c_{\rm s, NH_3}} \tag{6.42}$$

The ammonia concentration in the bulk is calculated as a radial mixing cup average one wire diameter in front of the respective wire and is scaled to the wire temperature. Following this procedure, a conversion weighted temperature of $\overline{T}_X = 1112.6$ K and a conversion weighted ammonia mass transfer coefficient of $\overline{\beta}_{\rm NH_3} = 0.93$ m s⁻¹ are obtained. The system of ODEs in Equation (6.38) is integrated using an explicit Euler scheme with a spatial discretization of 100 elements. Since the ODE system states an initial value problem, at the inlet of PFR conditions equal to the CFD model have been chosen according to Table 5.2. The respective code is implemented and evaluated in MATLAB 2017b.

The resulting mole fraction profiles of NH_3 , NO and N_2O throughout the reactor are plotted in Figure 6.3. To assess the quality of the surrogate model, the respective mole fractions obtained from the full CFD-model are also shown. As can be seen, the profiles of the two models match quite well, with deviations decreasing towards the reactor outlet. The one-dimensional reactor model captures all relevant features of the CFD model and can therefore be used for the parameter optimization presented in the next section.

6.4.3. Parameter optimization

Before the activation energies of the identified elementary steps are adjusted, the decomposition of N₂O needs to be suppressed. This is done rather straightforward by increasing the activation energy for reaction R21 (N₂O decomposition to N₂) from 154.7 kJ mol⁻¹ to 176 kJ mol⁻¹. For the given catalyst temperature of 1112.6 K, this raise in energy of $\Delta E_a = 21.3$ kJ mol⁻¹ equals a lowering of the rate constant by a factor of 10.

In the next step, the activation energies of reactions R17, R19 and R20 are fitted, such that the PFR model yields the target selectivities listed in Table 6.2. This is done using MATLAB's nonlinear optimization solver *lsqnonlin*. It solves a non-linear least squares problem by changing the parameters contained in x until the sum of squares of the target function f(x) is minimized:

$$\min_{x}(|f(\mathbf{x})|^2) = \min_{x}\left(\sum_{i} f_i(\mathbf{x})^2\right)$$
(6.43)

The target function $f(\mathbf{x})$ is a vector containing the differences between the target selectivities S_{tar} and the selectivities obtained from the one-dimensional PFR model S_{PFR} :

$$f(\mathbf{x}) = \begin{pmatrix} f_1(\mathbf{x}) = \Delta S_{\text{NO}} = S_{\text{NO,PFR}} - S_{\text{NO,tar}} \\ f_2(\mathbf{x}) = \Delta S_{\text{N}_2\text{O}} = S_{\text{N}_2\text{O,PFR}} - S_{\text{N}_2\text{O,tar}} \\ f_3(\mathbf{x}) = \Delta S_{\text{N}_2} = S_{\text{N}_2,\text{PFR}} - S_{\text{N}_2,\text{tar}} \end{pmatrix}$$
(6.44)

The vector \mathbf{x} contains the parameters to be optimized, i.e. the activation energies of reactions R17, R19 and R20:

$$\mathbf{x} = \begin{pmatrix} E_{\mathrm{a},17} \\ E_{\mathrm{a},19} \\ E_{\mathrm{a},20} \end{pmatrix}$$
(6.45)

Once the optimized activation energies are obtained, the CFD model was re-run with the new kparameters. The altered parameters and the resulting integral selectivities from the CFD simulation are listed in Table 6.4. With the altered kinetic model, the obtained selectivities slightly deviate from the target selectivities. This is primarily caused by a drop in catalyst temperature: The selectivities are slightly shifted towards the main product NO, mainly on the expense of N₂O, and thus the heat released by chemical reaction also slightly decreases, as the reaction towards NO per mole of NH₃ consumption is less exothermic ($\Delta_{\rm R}H^{\circ} = -226$ kJ mol⁻¹) than the formation of N₂O ($\Delta_{\rm R}H^{\circ} = -368$ kJ mol⁻¹).

In a more advanced approach, one could also solve for the wire and bulk temperature by extending the PFR model with a heat balance equation. In this work, the predicted parameters have turned out to be suitable initial values for a manual optimization using the full CFD model. This manual adjustment takes only a few iterations and leads to the desired integral selectivities as illustrated in Table 6.4. The adjusted kinetic model obtained from this final optimization will from now on be used for all further investigations within in this chapter.

Table 6.4.: Results of the parameter optimization. Shown are the original parameters, the parameters obtained
from MATLAB's *lsqnonlin* solver and the parameters from the manual optimization in the CFD model.
For all three kinetic models the integral conversion and product selectivities, as well as the gas
temperature at the outlet of the CFD model are listed.

Parameter	Original	Matlab optimized	CFD optimized	
$E_{\mathrm{a},17}$ / kJ mol $^{-1}$	121.2	124.4	124.4	
$E_{\mathrm{a},19}$ / kJ mol $^{-1}$	79.1	78.6	79.5	
$E_{\mathrm{a},20}$ / kJ mol $^{-1}$	92.9	107.2	106.8	
$E_{\mathrm{a},21}$ / kJ mol $^{-1}$	154.7	176.0	176.0	
$X_{\rm NH_3}$ / %	99.83	99.83	99.83	
$S_{\rm NO}$ / %	93.85	95.91	96.00	
$S_{ m N_2O}$ / %	3.69	1.51	1.60	
$\bar{S_{N_2}}$ / %	2.46	2.58	2.40	
$T_{\rm out}$ / K	1118.1	1115.4	1115.0	



Figure 6.4.: NH₃- and product species mass fraction field as well as temperature field from the CFD calculation with the optimized kinetic model.

As previously outlined, the activation energy of R21 (N₂O(s) \rightleftharpoons N₂ + O(s)) has been increased by 21.3 kJ mol⁻¹ to suppress N₂O decomposition. Most of the selectivity shift is gained by raising the energy barrier of R20 (NO(s) + N(s) \rightleftharpoons N₂O(s) + Pt(s)) by 13.9 kJ mol⁻¹, which reduces N₂O formation mainly in favor of NO formation. Only a small elevation in activation barrier of 3.2 kJ mol⁻¹ is needed for R17 (N(s) + O(s) \rightleftharpoons NO(s) + Pt(s)) and a raise of 0.4 kJ mol⁻¹ for R19 (N(s) + N(s) \rightleftharpoons N₂ + Pt(s)). With a maximum increase in activation energy of about 20 kJ mol⁻¹, the adjusted values lie within the typical accuracy of activation energies that are determined from DFT calculations [147].

The profiles of species concentration and temperature obtained from the CFD model with the adjusted mechanism are shown in Figure 6.4. It can be seen that all the relevant features are preserved in the model while there is no decomposition of N_2O anymore occurring at the rear wires.

6.5. Combining flow simulations with sensitivity analysis of mass transfer limited surface kinetics

So far, the concept degree of rate control for a surface mechanistic model with external mass transfer, as well as an adjusted microkinetic model for industrial ammonia oxidation have been presented.

In this section the effect of including mass transfer into the kinetic model will be discussed. Afterwards, the degree of rate control with different detail levels of included mass transfer is investigated. Furthermore, the performance of the numerical and analytic evaluation of the degree of rate control with external mass transfer is elucidated.

The main focus of this section lies in the combination of degree of mass transfer control analysis with resolved CFD reactor simulations to predict the N_2O and N_2 selectivity as a function of local mass transfer. This novel tool for catalyst characterization is then applied to study different catalyst models, i.e. the two-dimensional single wire, two-dimensional multi-wire configuration and three-dimensional crossed wires. Finally three-dimensional woven gauze, as well as a restructured wire based on CT-images, where the microscale of the catalyst is explicitly resolved, are investigated.

6.5.1. Degree of rate control analysis with mass transfer

Figure 6.5 shows the full degree of rate control analysis of the adjusted microkinetic model with mass transfer, evaluated using the analytic method. The gas composition in the bulk is the same as the inlet composition for the 10-wire reactor model. Catalyst temperature (T = 1115 K) as well as the mass transfer coefficient for NH₃ ($\beta_{\rm NH_3} = 0.95$ m s⁻¹) were taken from the CFD solution, extracted at the tip of the front wire.

The high sensitivity of the net rates with respect to the mass transfer coefficients of the gas species indicate that the system is controlled by external mass transfer. This is in line with the CFD results of the reactor model, where strong concentration gradients around the catalyst wires are observed.

Compared to the changes in the rate constants of the surface reaction steps, the system is much more sensitive to changes in mass transfer, stating that mass transfer is the rate-limiting process. The response of the NO formation rate is quite low compared to the production rates of the by-products. This can be explained by the fact, that $S_{\rm NO} > 90\%$ and therefore the rate is already very high, thus leading only to small relative changes in NO formation rate. In contrast, the rates of N₂O and N₂, which are significantly lower in absolute values, exhibit higher sensitivity coefficients.

The transfer of NH₃ to the catalyst is rate-limiting ($X_{\rm RC}^m > 0$) for the rates of all product species. This is expected, as NH₃ is the limiting compound from which the formation pathways of all three species originate. Decreasing its rate of transportation to the surface would decrease the formation rates of all three product species. With respect to the by-products, oxygen transfer to the surface and NO removal from the surface are both inhibiting processes, lowering the formation rates of N₂ and N₂O.

The ratio of product formation rates is determined by the ratio of surface coverages of N(s), O(s) and NO(s): A surface nitrogen can either react with another nitrogen via R19 (N(s) + N(s) \rightleftharpoons N₂ + Pt(s)) or combine with a surface NO to form N₂O via R20 (NO(s) + N(s) \rightleftharpoons N₂O(s)). NO(s) is formed by R17 (N(s) + O(s) \rightleftharpoons NO(s)) and can desorb from the surface via R18 (NO(s) + N(s) \rightleftharpoons N₂O(s)).

If the coverage of surface nitrogen is raised, the probability for all three combination pathways increases and thus the net rate for all three species is pushed. At the same time, an increase in oxygen surface coverage, due to a higher mass transfer rate of gaseous oxygen, blocks surface sites and decreases N(s) coverage. This has two consequences: First, a surface N(s) is more likely to react with surface oxygen to NO instead of combining with another nitrogen. Second, the probability of a NO(s) to desorb from surface before reacting with a N(s) increases. Thus, these two effects both favor the formation



Figure 6.5.: Degree of rate control of the adjusted kinetic model with mass transfer (X_{RC}^m) evaluated for conditions at the tip of the front wire of the 10-wire CFD model.

of NO. Why an enhanced NO mass transfer inhibits formation of N_2O is given by similar reasoning: The more NO molecules can leave the surface per unit time, the lower the NO(s) coverage and thus the lower the probability of a NO(s) reacting with a N(s). A lower NO coverage also inhibits the decomposition reaction of NO(s) and in turn reduces N(s) coverage. The lower coverage also deceases the N_2O formation rate and furthermore explains the negative correlation between N_2 production rate and NO mass transfer intensity.

Turning towards the surface reactions, it can easily be seen that only a small number of reactions

show a significant X_{RC}^m . Similar qualitative results as for the influence of mass transfer can be found for the adsorption/desorption reactions for NH₃ and O₂ (R1 and R2), although exhibiting much smaller sensitivities. Adsorption of NH₃ is rate-limiting for the formation of the side products, while O₂ adsorption is inhibiting. The explanation for the behavior of the X_{RC}^m for those two reactions is the same as given above, but due to mass transfer limitations, the numerical values are significantly smaller compared those obtained for the mass transfer sensitivity.

From the remaining elementary steps only R17 (N(s) + O(s) \Rightarrow NO(s)), R19 (N(s) + N(s) \Rightarrow N₂ + Pt(s)) and R20 (NO(s) + N(s) \Rightarrow N₂O(s)) are of significance. Again, the $X_{\rm RC}^m$ for N₂ and N₂O is higher than for NO. If one looks at the individual reactions and the sign of $X_{\rm RC}^m$, the results are well within the frame of expectation. Unlike the mass transfer of NO, the elementary step describing NO adsorption (R18) does not contribute to $X_{\rm RC}^m$, as with a partial equilibrium of $r_{\rm f}/r_{\rm b}$ = 0.998 this reaction is almost in chemical equilibrium. Despite the size and complexity of the mechanistic model, only a few elementary steps are rate-limiting or inhibiting, which is in agreement with observations from classical degree of rate control analysis of other surface kinetic models neglecting mass transport effects [116].

6.5.2. Performance of evaluating the degree of rate control with mass transfer

As presented in sections 6.3.3.1 and 6.3.3.2, the degree of rate control can be evaluated either numerically or analytically. For a surface kinetic model with mass transfer, the numerical evaluation requires the integration of the full set of DAEs once for every rate constant and mass transfer coefficient. With nR reactions and nG gas species, the corresponding numerical DAE solver has to be invoked (nR + nG + 1) times for the full degree of rate control analysis. For the analytic evaluation on the other hand, only one call of the DAE solver is required to generate the reference solution.

The Jacobians in Equation (6.37) can be obtained from a converged solution with little effort. From section 6.3.3.2 it can be seen, that for the four Jacobians a total of $(nS + nG + nR) \cdot (nS + nG)$ partial derivatives have to be calculated. Even though this seems to be a large number of evaluations, in most cases the computation of all Jacobians is still less demanding than one call of the DAE solver.

In order to compare the performance, both approaches were used to calculate the degree of rate control for the adjusted microkinetic model with mass transfer. The partial derivatives for the Jacobians were evaluated using a *central difference scheme*. All calculations were conducted in MATLAB 2017b [149]. For the time evaluation, MATLAB's functions *tic* and *toc* were used. In order to obtain a reasonable average, the calculations were repeated for 100 randomly chosen bulk gas compositions and catalyst temperatures. The random compositions were generated by choosing NH₃ mole fractions between 0.09 and 0.12 and then balancing with air (21% O₂ and 79% N₂) and the temperature was randomly varied between 1050 K and 1220 K. For every run, a reference solution was generated and the full $X_{\text{RC},i,j}^m$ including the corresponding $X_{\text{SC},i,j}^m$ for NO, N₂O and N₂ via Equation (6.21) were calculated. All computations were conducted in serial on a machine with an Intel Core i5-6500 CPU @ 3.2 GHz, 32 GB of RAM and Microsoft Windows 10 64-bit as an operating system. The total time required for all 100 runs, as well as the average time per run are listed in Table 6.5.

Table 6.5.: Total and average time for numerical and analytic evaluation of $X_{\rm RC}^m$ and $X_{\rm SC}^m$.

Method	Total time / s	Time per run / s
Numerical	383.7	3.837
Analytical	19.8	0.198

The total time required for 100 numerical evaluations was 383.7 s, yielding an average of 3.837 s per run. The total time for all analytic evaluations took 19.8 s, with an average of 0.198 s per run.

The solution accuracies were assessed using the summation rule in Equation (6.19). Although the accuracy of analytic solution tends to be higher, the difference in the calculated values between the two methods is negligible. The results show clearly, that the analytic evaluation requires only a fraction of the time compared to the numerical method. A more detailed look reveals that, on average, one integration of the DAE system takes 128 ms, while the computation of all four Jacobians requires only 65 ms. Inverting the matrix took about 0.1 ms. While for the analytic method per run only one call of the DAE solver and one calculation of the Jacobians are required, the numerical method demands a total of 30 (22 rate constants + 7 mass transfer coefficients + reference solution) DAE solver calls per run, thus explaining the vast speedup of the analytic evaluation by a factor of almost 20. This speedup is expected to be more pronounced when dealing with mechanisms exhibiting even larger numbers of reactions and species. At first glance this may seem contradictory, as the number of partial derivatives grows faster with the size of the kinetic model than the number of algebraic and differential equations which need to be solved. However, systems with more reactions and species tend to be more "stiff" and thus numerically more demanding to integrate, since the DAE solver needs more steps to reach a certain accuracy of the solution. Usually, the increasing stiffness of the system outweighs the effect of faster growing number of partial derivatives to be evaluated. The analytic approach of course is not limited to degree of rate control type analysis. The adaption to reaction and selectivity orders for example is straightforward. In principle, the analytic evaluation can be used for any sensitivity analysis of kinetic systems in steady state.

6.5.3. Including mass transfer effects on different levels of detail

In this section, the necessity of accounting for mass transfer effects in a degree of rate control analysis is demonstrated.

Four scenarios are presented, where mass transfer effects are accounted for with increasing level of detail. It is shown, how a degree of rate control analysis may lead to incorrect results, when these effects are neglected. The discussion will be limited to the selectivity towards N_2O . Figure 6.6 shows the degree of selectivity control for N_2O for the four different cases:

In (a) the microkinetic model without mass transfer is analyzed using the bulk gas concentrations which match those at the inlet of the reactor model (see Table 5.2). In (b) the same analysis is performed, but this time with more realistic gas concentrations, which are taken directly from the solution of the 10-wire CFD model. The values are extracted at the tip of the first wire. Case (c) shows the degree of selectivity control with mass transfer and in (d) the analysis is performed directly with the full CFD model of the 10 wire configuration. In all cases a catalyst temperature of $T_{\rm s} = 1115$ K was used.

First, the two analyses without mass transfer, i.e. cases (a) and (b), are discussed. The differences in the results between the two models are very pronounced. Not only does the sensitivity for almost every elementary step with significant sensitivity differ strongly. For most reactions even the sign of X_{SC} flips, which means that reactions that have been rate-limiting now become inhibiting or vice versa. Only for the reaction describing the formation of surface N₂O, almost equal sensitivities are predicted. Interestingly, the increase in adsorption rate of NH₃ and O₂ exhibits completely opposite tendencies for the selectivity. When using the bulk concentrations in case (a), against all the previous findings, enhanced ammonia adsorption is decreasing N₂O selectivity. It is not less surprising that enhanced O₂ adsorption increases N₂O selectivity. This is explained by the relatively high coverage of N(s) which is caused by high concentration of NH₃ in the gas phase close to the surface and low NO(s) coverages. Intensifying the ammonia adsorption and thus raising the N(s) coverages favors formation of N₂ at the expense of NO(s) formation. As the formation rate of N₂O is controlled by the NO coverage, this leads to a decrase in N₂O selectivity. Increasing the adsorption rate of oxygen on the other hand



Figure 6.6.: Degree of selectivity control for N₂O evaluated at T = 1115 K. (a) Only chemistry without mass transfer is considered, performed using the gas bulk concentrations equal to the inlet concentrations of the CFD model listed in Table 5.2. (b) Same as (a) but this time the concentrations at the tip of the first wire from the 10-wire CFD model are used. (c) Chemistry and mass transfer are considered. (d) With the 10-wire CFD model, performed at the tip of the first wire.

causes the opposite effect, as it strongly promotes NO(s) formation due to elevated O(s) coverages, thus increasing N_2O selectivity. These results show, that the sensitivity of the kinetic system strongly depends on the conditions chosen in the gas phase. As a consequence, the results of such an analysis may vary throughout a reactor due to changing composition, even when operated outside the mass

transfer controlled regime. All in all, the two models predict a completely different behavior of the surface kinetic system.

Despite having information about the near-surface concentrations, this is only half of the story. During the calculation of the sensitivities in case (b), the gas concentrations are still kept fixed and changes in gas phase composition close to the catalyst surface due to variation of kinetic parameters are still omitted.

The discussion proceeds with case (c), where the microkinetic model including mass transfer is investigated. Since the DAE system given by Equations (6.15) and (6.16) is solved for the near-surface concentrations, the above mentioned concentration changes, caused by the perturbation of kinetic parameters, are included within the analysis. As described in section 6.3.2, by altering the mass transfer coefficients, one obtains information on how changes in mass transfer rates affect the overall selectivities. The NH₃ mass transfer coefficient is extracted from the CFD solution of the 10-wire model directly at the tip of the first wire. The sensitivities with respect to the mass transfer coefficient of each individual gas species are lumped together into a single coefficient accounting for the effect of the overall mass transfer. Accounting for mass transfer effects, the most distinctive result is that the N_2O selectivity becomes less sensitive towards the adsorption of NH₃ and O₂ compared to case (b). This is expected, as in case (c) the mass transfer now precedes adsorption and both steps are connected in series. With the first step being rate limiting, the sensitivity of the subsequent step decreases. With the near-surface concentrations not being fixed anymore, increasing the rate constant for the species adsorption, the near-surface concentrations of NH₃ and O₂ slightly drop. To a certain extend they compensate for the increased rate coefficient, as the rate of adsorption is proportional to the near-surface concentrations. Although, the adsorption rates in total increase, this increase is less pronounced as in case (b), where the near-surface concentrations are kept constant. As a consequence, the N(s) and O(s) surface coverages do not change as much.

It has become clear from the preceding discussions, that the product selectivities are determined by the relative rates of the reactions of N(s) with NO(s), O(s) or another N(s), which itself are mostly determined by the surface coverages of N(s) and O(s). This explains the values for X_{SC}^m obtained, when mass transfer effects are considered. The changes in selectivity with respect to the three recombination reactions leading to the formation of NO(s), N₂ and N₂O(s) are also shifted, although not as distinctive as for the adsorption reactions. Altogether, both scenarios predict the same tendencies for the behavior of the kinetic model, since the sign of X_{SC}^m is the same for all elementary steps in both cases.

So far, the discussion has not yet covered the direct influence of changes in mass transfer on the overall product selectivities which, in case of the N_2O selectivity, is described by the topmost bar in Figure 6.6c. Here, a positive value indicates that an increase in mass transfer coefficient leads to an increase in N_2O selectivity. This is valuable information, as one can immediately see, how the selectivity of a product responds to changes in mass transfer. In most cases the adjustment of local mass transfer can be realized comparably cheap and easy, for example by changing the flow velocity throughout the catalyst or by optimizing the shape of the catalyst itself. Thus, the selectivities of a catalytic system can be controlled, without having to change the catalyst in its chemical composition, which very often is complex and time consuming.

Figure 6.6d shows the degree of selectivity control obtained with the full CFD model of the 10-wire configuration. The analysis is conducted at the tip of the first wire. To obtain the different X_{SC}^m , the different kinetic constants were changed by a factor of h = 1.001. Then a full CFD simulation was performed for every altered parameter and the respective chemical rates where extracted from the solution. For better comparability, the temperature of the wires was fixed to $T_s = 1115$ K. To asses the sensitivities with respect to mass transfer, an additional simulation was carried out increasing the inlet velocity by a factor of h = 1.001. This leads to an increase in NH₃ mass transfer coefficient by

a factor of 1.0004. This is in line with the previous argumentation where $Sh \sim Re^m$ with m varying between 0.33 and 0.4 for a cylinder in cross flow. The respective partial derivatives were approximated using Equation (6.28). This approach represents the most "advanced" form for a degree of rate control analysis, as it allows to investigate the behavior of the surface kinetics in a sophisticated reactor model which resolves the geometry of the catalyst, as well as concentration- and temperature gradients. A very interesting result is that with this *reactor-scale* degree of rate control almost the same results are obtained as with the kinetic model including mass transfer in case (c). This allows to perform a full featured degree of rate rate control analysis, that contains the necessary mass transfer effects, at almost equal level of accuracy, but only at a fraction of the numerical effort. It has to be emphasized, that compared to an conventional CFD simulation, the reactor-scale degree of rate control requires a very high solution accuracy and strong convergence criteria due to the small changes in kinetic parameters and mass transfer intensity.

6.5.4. Flow simulations and degree of mass transfer control analysis as a combined tool for catalyst characterization

In the previous sections the necessity to incorporate mass transfer effects into a degree of rate control analysis was demonstrated. The concept of degree of mass transfer control was introduced as a method to quantify the response of chemical kinetics and product selectivity to changes in external mass transfer. To obtain information on the distribution of mass transfer intensity on the catalyst surface, simulations of more complex catalyst structures will be conducted. The CFD simulations will be combined with degree of mass transfer control analysis and the potential of this combined approach for rational catalyst design will be illustrated.

6.5.4.1. Two-dimensional single wire

One of the main observation from the detailed simulations in the previous chapter was that the local N_2O selectivity varied along the surface of the different catalyst wires. This was attributed to the changing distribution of near-surface NH_3 concentration, caused by different mass transfer rates of NH_3 along the surface due to the characteristics of flow and catalyst. With the degree of mass transfer control analysis one has at hand a tool which directly relates the changes in local mass transfer with the resulting changes in species net rates and selectivities. In contrast to the discussions in the previous chapter, this is a more direct and elegant approach to explain the catalyst performance, as the change of near-surface concentrations are a consequence of changing mass transfer intensity and are implicitly treated within the degree of mass transfer analysis.

Another advantage of arguing in terms of mass transfer coefficients is that they are independent of the kinetic model being used. Furthermore, they constitute a physical parameter that can easily be controlled by chemical engineers and plant operators, as it is directly related to the flow configuration and the geometry of the catalyst.

In the next step, the surface kinetic model is investigated using simulations of the single wire geometry of Figure 5.1 for the standard conditions in Table 5.2. Local mass transfer coefficients for the chemical species can be calculated from a converged solution using the following equation:

$$\beta_i = \frac{J_i}{c_{\mathrm{b},i} - c_{\mathrm{s},i}} \tag{6.46}$$

As bulk concentration, the concentration at the inlet of the domain is chosen and scaled to the wire temperature. Figure 6.7a shows the selectivity of N_2O and N_2 , as well as the NH_3 mass transfer coefficient

along the perimeter of the wire. The mass transfer coefficient shows a maximum at the stagnation point of the wire and declines moving to the rear of the wire. Due to the flow field around the wire, the concentration boundary layer increases towards the rear part of the wire (see Figure 5.3), increasing the mass transfer resistance. The selectivities of N₂O and N₂ correlates with the intensity of the mass transfer, i.e. they also exhibit a maximum at the stagnation point and decreases towards the back of the wire. Furthermore, it is evident that the positive dependence on the mass transfer is much more pronounced for the formation of N₂ than for NO. These observations are also predicted by the degree of mass transfer analysis shown in Figure 6.7b. The calculations were performed with the conditions prevalent at the tip of the single wire, i.e. T = 1116 K and $\beta_{\rm NH_3} = 0.96$ m s⁻¹. For the selectivity of both side products, a positive $X_{\rm SC,\beta}^m$ is obtained. In addition, the sensitivity coefficient for N₂ selectivity is about three times higher, indicating a higher dependency on the mass transfer rate. The same qualitative result is obtained directly from the CFD solution. The negative coefficient for NO indicates that its selectivity is decreasing when mass transfer is amplified, which is expected as the selectivity of the remaining two products is increases.



Figure 6.7.: (a) N₂O selectivity, N₂ selectivity and NH₃ mass transfer coefficient along the perimeter of the single wire. (b) Degree of mass transfer control for the selectivity of the product species. The analysis is performed with the temperature and mass transfer coefficient taken from the tip of the single wire.

Qualitatively the CFD model and the degree of mass transfer analysis yield identical results. To check the results in a more quantitative manner, some rough estimations can be done: The mass transfer coefficient decreases by approximately 62% when moving from the front to the rear side of the wire. With $X_{SC,\beta}^m \approx 0.43$ for N₂O, an approximate relative decrease in selectivity by $0.43 \cdot 62\% = 26.7\%$ would be expected. Looking at the change in N₂O selectivity in Figure 6.9a, it can be seen that the N₂O selectivity falls from 2.00 to 1.42%, which indeed equals a relative decline by 29%. For N₂, with a $X_{SC,\beta}^m \approx 1.53$, the relative increase in selectivity forecasts to $1.52 \cdot 62\% = 94.2\%$. This estimation is a slightly too high, as the N₂ selectivity does change only from 4.04% to 1.10%, which corresponds to a relative decline of only 73%. However, one should be aware that a linearization was used for the estimations above (i.e. fixed values of X_{SC}^m were assumed along the perimeter of the wire) with a sensitivity analysis based on the mass transfer coefficient extracted at the tip of the wire. Since β_{NH_3} does change along the perimeter of the wire, the sensitivity coefficients are expected to do as well.

The $X^m_{SC,\beta}$ for the three product species as a function of NH₃ mass transfer coefficient for a fixed

temperature is shown in Figure 6.8. The mass transfer coefficients of the remaining species have been scaled according to Equation (6.14). The sensitivities for N₂O and NO selectivity both show a maximum for $\beta_{\rm NH_3} = 0.8 \mbox{ m s}^{-1}$, and decline if mass transfer is further intensified. It can also be observed, that when moving towards lower values of $\beta_{\rm NH_3}$, the degree of mass transfer control does drop faster for N₂O than for N₂O. This stronger dependency explains, why the N₂ selectivity is overestimated while N₂O selectivity is calculated slightly too low, when using the linearization as done above.

Though the sensitivities change over the whole range of β_{NH_3} displayed in Figure 6.8, the sign is conserved for all three species, i.e. lowering mass transfer resistance will lead to an increase in side product selectivity over the whole range of mass transfer intensity.

At this point it has to be noted, that though the mass transfer coefficients in the analysis have been taken from a CFD solution with the full kinetic model, the solution of the full model is not required. Solving the system with a Dirichlet boundary condition for NH_3 concentration ($c_{NH_3} = 0$) or a simple fast first order reaction with respect to NH_3 at the catalyst surface instead of the full kinetics is a sufficient way to obtain local mass transfer coefficients.



Figure 6.8.: Degree of selectivity control with respect to the overall mass transfer for N₂O, N₂ and NO as a function of NH₃ mass transfer coefficient.

6.5.4.2. Two-dimensional multi-wire configuration

In this section, the correlation of mass transfer and product selectivity is investigated using the 10-wire configuration of Figure 5.7. The simulation was conducted for the standard conditions of Table 5.2. The resulting side product selectivity and the NH_3 mass transfer coefficient along the perimeter of the first four catalyst wires are displayed in Figure 6.9. Concerning N_2O , the picture is qualitatively the same as obtained with the microkinetic model from Kraehnert: The selectivity changes around the circumference of the individual wires with a maximum at the front and declining towards a minimum at the rear of the wire. Also in line with the previous results, the highest selectivity is observed at the stagnation point at the tip of the second wire. Including the N_2 selectivity in Figure 6.9b into the discussion, it is observed that for all individual wires the variation of selectivity is much more pronounced in this case. This result was already obtained for the single wire case.

From Figure 6.9c it is evident that also the local mass transfer coefficient varies along the perimeter of each wire. In general, the mass transfer intensity declines moving towards the rear wires. An exception from this trend is found for the second wire, which exhibits the highest mass transfer coefficient of all



Figure 6.9.: (a) N₂O selectivity, (b) N₂ selectivity and (c) NH₃ mass transfer coefficient plotted along the perimeter of the different wires in the 10-wire model. Operating conditions are identical to the standard conditions of Table 5.2.

wires. An explanation for this enhancement in mass transfer rate was already given in section 5.4.3: When passing the first row of wires the flow is channeled and accelerated towards the wires of the second row, which are located directly behind the gap of the first row. This acceleration is on one hand caused by the narrowing of the cross sectional area, on the other hand the gas expands as heat is transferred from the hot wire to the cold gas. Thus the flow impinges the second wire with a higher velocity than the first wire, leading to a higher mass transfer coefficient on the frontal area of the second wire.

Again, once information on the change in local mass transfer is obtained, the distribution of product selectivity can be described by a degree of mass transfer control analysis. The analysis, conducted for conditions at the tip of the first wire, yields almost identical results as for the single wire in the previous chapter. Therefore, for the proceeding discussions on the influence of mass transfer the results in Figure 6.7b are utilized. As already pointed out, the analysis predicts a positive response of the side product selectivities with respect to changes in mass transfer. This behavior is also reflected by the results of the full CFD model, where a clearly positive correlation between mass transfer coefficient and

side product selectivity is obtained. The more pronounced variation in N₂ selectivity along an individual wire, as well as between the individual wires is captured by the sensitivity analysis, predicting $X_{SC,\beta}^m$ to be three times larger for S_{N_2O} than for S_{N_2O} .

It can be concluded, that the maxima in selectivity on the second wire should be robustly predicted for every kinetic model exhibiting a positive sensitivity of product selectivity with respect to mass transfer.

It should be noted, that in the CFD simulation the wire temperature was not fixed, so the temperature of the first wire was increased compared to the downstream wires. Thus, the difference in the selectivity between the different wires is not a pure effect of mass transfer and species concentration, but also a function of temperature. The simulation predicts a temperature difference between the first and the second wire of about 11 K.

6.5.4.3. Three-dimensional crossed wires

In this section, the investigations are extended to a three-dimensional gauze catalyst model, which is a step forward towards a real gauze catalyst shape. The geometry, representing a model of a woven gauze catalyst, is shown in Figure 6.10. The diameter of the wires is $d_w = 100 \mu m$ and the wires in each layer are oriented perpendicular to the ones in the previous layer. The center-to-center distance between two parallel wires is $3d_w$. A pair of subsequent horizontal and vertical parallel wires represents one layer of a woven gauze. Every gauze layer is shifted by $1.5d_w$ in horizontal and vertical direction with respect to the upstream layer, i.e. each layer of parallel wires is in an staggered configuration with respect to the second-next layer.



Figure 6.10.: Left: Geometry of the catalyst approximated as layers of parallel wires, with the wires in one layer oriented perpendicular with respect to the wires in the next layer. Each pair of layers is in staggered configuration with respect to the next pair. Wire diameter is $d_w = 100 \mu m$, center-to-center distance between to parallel wires is $3d_w$. There is a gap of $0.1d_w$ between each individual layer of parallel wires to avoid singular contact points. Due to symmetry, only the domain inside the blue cuboid needs to be taken into account. Right: Frontal view on the wire configuration.

To avoid singular contact points, there is a gap of $0.1d_w$ between each individual layer of parallel wires. Due to symmetry of the configuration, only the domain inside the blue cuboid needs to be taken into account in the simulations. The standard operating conditions of a medium-pressure plant as presented in Table 5.2 are used for the calculations.



Figure 6.11.: Temperature- and NH₃ mole fraction along two *xy*-planes.

Figure 6.11 shows the computed temperature- and NH_3 mole fraction field along two *xy*-planes. The results are in line with the expected behavior of an exothermic and mass transfer limited adiabatic process, as previously discussed for the two-dimensional case. The ammonia concentrations near the surface is close to zero, leading to pronounced gradients in mass fraction around the catalyst wires. These gradients result in an almost full NH_3 consumption already after the first few wires. Furthermore, strong temperature gradients can be observed, causing the initially cold gas to heat up when passing the hot catalyst wires.

Figure 6.12 shows the local distribution of product selectivities (top row) and NH_3 mass transfer coefficient on the surface of the catalyst (bottom left), as well as the degree of mass transfer control (bottom right). For the sensitivity analysisv the temperature and the mass transfer coefficient from the center of the front side of the first wire have been used. In agreement with earlier results, higher mass transfer coefficients are in general observed on the front wires compared to the rear wires. Also in line with the results from previous two-dimensional investigations are the observations of higher mass transfer intensity on the front surfaces of the wires relative to the rear surface. A new phenomenon that occurs only in three-dimensional configurations is the shadowing effect of an upstream wire on the subsequent orthogonal aligned downstream wire. This leads to very low mass transfer coefficients on surface areas of that are shadowed by an upstream wire.

Another interesting result is that for the three-dimensional gauze the highest mass transfer coefficients and N_2O selectivity are now found on the frontal surface of the third wire. This is due to a flow effect caused by the first two rows of wires. The first layer of wires directs the flow in y-direction (the main flow is in x-direction), leading to a stagnation point of increased mass transfer on the second wire, right in the center between the two upstream wires. The second row of parallel wires once more confines the flow but now in z-direction, leading to further acceleration of the flow and resulting in an even more pronounced stagnation point on the third wire. This stagnation point with highest velocity gives rise to the observed maximum in NH₃ mass transfer coefficient on the third wire.

Again, the positive degree of mass transfer control of the side product selectivities explains the correlation of points of high N₂O and N₂ selectivity with points of high local mass transfer coefficient. The same rationale can be applied to explain the distribution of NO selectivity, but this time a negative $X_{SC,\beta}^m$ leads to lower selectivities on points of increased mass transfer. Furthermore, the stronger dependence of N₂ selectivity with respect to mass transfer, as predicted by the degree of mass transfer control, is manifested in the results of the CFD model, as in Figure 6.12 the range in which the selectivities



Figure 6.12.: Top: Local NO-, N₂O- and N₂ selectivity on the catalyst surface from the CFD simulation with the full microkinetic model. Bottom left: Local NH₃ mass transfer coefficient on the surface of the catalyst. Bottom right: Degree of mass transfer control for NO-, N₂O- and N₂ selectivity. For the analysis the temperature and NH₃ mass transfer coefficient at the front of the first horizontal wire has been used.

vary across the catalyst surface is again much larger for N₂ than for N₂O. As it was argued for the two-dimensional simulations, the maxima in side product selectivity should be robustly predicted by any microkinetic model with a positive $X_{SC,\beta}^m$ for N₂O and N₂ selectivity.

6.5.4.4. Detailed analysis with selectivity orders

As demonstrated in the previous sections, the local selectivities towards the products are functions of local mass transfer. Intensified mass transfer rates favor the production of the unwanted by-products N_2O and N_2 . If instead, the external mass transfer coefficient is decreased, the selectivity towards the desired product NO is increased. To get a better understanding of this phenomenon, the effect of species concentrations near the catalyst surface is investigated. As the local mass transfer coefficient is changed, the system adjusts to a new set of near-surface concentrations, given by the solution of Equations (6.15) and (6.16). With the resulting concentrations, the effect of the changes in surface concentrations on the product selectivity can be computed. Mathematically speaking, this is applying the chain rule to the

degree of mass transfer control:

$$\frac{\beta}{S_i}\frac{\partial S_i}{\partial \beta} = \frac{\partial \ln S_i}{\partial \ln \beta} = \sum_j \frac{\partial \ln c_j}{\partial \ln \beta}\frac{\partial \ln S_i}{\partial \ln c_j} = \sum_j \frac{\partial \ln c_j}{\partial \ln \beta} n_{S_i,j}$$
(6.47)

Note that the second factor in the sum in Equation (6.47) is the selectivity order, that was introduced in Equation (5.7). For the calculation of the normalized changes in near-surface concentrations with respect to the mass transfer coefficient, the microkinetic model with mass transfer needs to be utilized. The temperature and mass transfer coefficient are taken from the tip of the first wire of the CFD solution. With the respective near-surface concentrations at hand, the selectivity orders can be determined using the simple kinetic model without mass transfer. Table 6.6 shows the calculated partial derivatives of Equation (6.47).

 Table 6.6.: Normalized changes in near-surface concentrations with respect to mass transfer coefficient and selectivity orders.

	NH ₃	O ₂	H ₂ O	NO	N_2O	N_2	H ₂
$\frac{\partial \ln c_j}{\partial \ln \beta}$	0.7093	0.1911	-0.0416	-0.1587	0.3565	0.0068	0.5395
$n_{S_{ m NO},j}$	-0.2708	0.2512	-0.0114	-0.1677	0.0000	0.0000	0.0000
$n_{S_{N_2O},j}$	1.4196	-1.7304	0.0591	1.7168	-0.0089	0.0000	0.0000
$n_{S_{\mathrm{N}_2},j}$	3.3518	-2.9243	0.1408	1.7015	0.0040	0.0001	0.0000

The concentration of NH₃ at the catalyst surface shows the highest sensitivity with respect to changes in mass transfer, which exceeds the value obtained for c_{O_2} by a factor of about 3.5. Both concentrations increase with higher β , while the NO concentration decreases. The selectivity orders of NO with respect to the concentrations of all species are significantly lower than the orders of N₂O and N₂, leading to the small negative overall value of $X_{SC,\beta}^m$ for NO (see Figure 6.12). N₂O and NO both show significant selectivity orders with respect to the concentrations of NH₃, O₂ and NO. While the selectivity orders of N₂O and N₂ with respect to c_{NO} are almost the same, the dependency of the N₂ selectivity on the concentration of ammonia and oxygen is more than twice as strong as for N₂O. This explains the huge difference in the value of $X_{SC,\beta}^m$.

Changes in concentrations of all other species (N₂O, N₂, H₂) do not contribute significantly, due to either negligible orders or small sensitivities with respect to mass transfer. In total, the large difference in the sensitivity of N₂O and N₂ selectivity with respect to β is mainly caused by a combination of the high sensitivity of $c_{\rm NH_3}$ to mass transfer (≈ 0.71) and the difference in the selectivity orders of N₂ (≈ 3.4) and N₂O (≈ 1.4) with respect to the concentration of ammonia.

As already discussed in section 5.4.6, the effect of near-surface ammonia concentration on the product selectivity is expected to be qualitatively predicted by the model. Furthermore, the increase in ammonia concentration with respect to mass transfer is a purely physical effect for a mass transfer controlled reaction. Since increased mass transfer mainly affects the near-surface concentrations of ammonia, the qualitative predictions of the degree of mass transfer control analysis can be regarded as robust.

6.5.5. Analysis of gauze structures

In this section the concepts determined in the previous sections will be applied to more complex models of gauze catalysts. The first part addresses a restructured catalyst wire, that has undergone the typical topological changes during operation, and its mass transfer characteristic at the microscale. Furthermore, a more sophisticated model for a woven gauze catalyst is investigated with focus on the effect of wire diameter and wire spacing.

6.5.5.1. Restructured wire based on CT images

During operation under industrial conditions the Pt/Rh catalyst wires undergo structural changes in the form of cauliflower-shaped excrescences that are growing on the catalyst surface. Due to the sensitivity of the product selectivity towards the catalyst shape, this reconstruction at the microscale are believed to have an influence on its performance.

Based on images from micro computer tomography (µCT), CFD simulations of a used wire segment with a marked reconstructed surface have been conducted. Therefore, two-dimensional image stacks obtained from the CT have been processed to obtain a CAD model of the wire using the commercial software ScanIP. The CAD model is then converted into a computational grid that can be used for flow simulations. The feasibility of this approach was first demonstrated by Wiser [132], who incorporated the detailed kinetic model from Kraehnert into the CFD simulations of a µCT-based wire model and compared the results to a smooth wire. He found that the restructured wire had a hydrodynamic diameter equal to that of a smooth wire with $d_w = 150 \mu m$. Furthermore, he reported that the reaction occurs mostly at the tip of the outgrowths, with the inner surface of the wire contributing little to the overall reaction. He also found that the tips of the cauliflower geometries exhibited an increased N₂O selectivity. Based on his observations, he concluded, that the surface enlargement should not be scaled simply by comparing physical surface areas. Instead, he suggested to use smooth wires with a diameter of 150 µm and to adjust the surface enhancement factor such that the simplified model matches the results (N₂O selectivity) obtained from the model of the restructured wire with a surface factor of 10. For a robust proposal of a suiting scaling factor however, further investigations of additional wire segments are needed, since Wiser only used one 0.3 mm long segment, resulting in a lack of statistical reliability.



Figure 6.13.: Computational domain for the restructured wire model. Main flow direction is along the *y*-axis.

The CT-images, that are used to construct the wire model, originate from a 300 μ m long wire segment of a gauze that was in operation for several hours. Figure 6.13 shows the domain of the wire model
with the outgrown structures being very pronounced and clearly visible. Compared to a smooth wire with a diameter of 100 μ m, the restructured wire model exhibits a surface area about twice as large. This area is about a factor of five lower than the value found reported in the literature, leading to the conclusion that there is still a significant sub- μ m structure that is not resolved in the CT-images. For the simulations, the conditions in Table 5.2 have been used. The main flow is in *y*-direction. To describe the surface kinetics, the adjusted Traversac model is implemented. Similar to the work of Wiser, a surface-enhancement factor of 10 is used. The resulting temperature and NH₃ mole fraction profiles are plotted in Figure 6.14.



Figure 6.14.: Temperature and NH₃ mole fraction profile around the restructured wire.

Due to the high thermal conductivity of the platinum, an almost homogeneous temperature profile throughout the whole wire is obtained and no significant temperature gradients between the inner part of the wire and the excrescences are observed. This result suggests that the proposed mechanism involving the Pt transport via gaseous PtO_2 from hotter parts of the wires to colder parts, giving a possible explanation for reconstruction, is unlikely to occur at the microscale. As expected, also with the micro-scale being resolved, heat and mass transfer limitations are still present, with strong temperature and concentration gradients being observed around the wire. Interestingly, the overall shape of the concentration- and temperature profile does not differ much from the one obtained for a smooth wire with diameter slightly larger than 100 µm. Due to the small length-scale of the cauliflower-shaped structures, no significant concentration and temperature gradients can be noticed around these structures. This supports the assumptions, that diffusion-effects on the microscale of the catalyst wire do not play an important role.

The distribution of local mass transfer coefficients on the catalyst surface is shown in the bottom left plot in Figure 6.15. At the inner sections of the wire, the mass transfer coefficient is almost zero, thus the contribution to the integral reaction is small. A completely reverse picture is obtained for the outgrowths, where the mass transfer is intensified. Here the mass transfer coefficient is even larger than on the stagnation points at the front side of the smooth wires. Due to their small characteristic length and the fact that they are more exposed to the flow, the mass transfer resistance around these more external structures decreases. The degree of mass transfer control is plotted in the bottom right of Figure 6.15. Combined with the distribution of local mass transfer, the predictions can again be compared to the profiles of local product selectivity, obtained from the flow simulations with the full

chemistry, displayed in the top row of Figure 6.15. Areas of high local mass transfer, together with a positive degree of mass transfer control, lead to increased local N₂O and N₂ selectivities around the tips of the cauliflower structures. Furthermore, this causes the side product selectivity to decrease in deeper areas closer to the wire center, where smaller mass transfer coefficients are observed. Similar to the smooth wires, the opposite behavior is found for the NO selectivity, as it exhibits a negative $X_{SC,\beta}^m$.



Figure 6.15.: Top: Local NO-, N₂O- and N₂ selectivity on the surface of the restructured catalyst. Bottom left: Local NH₃ mass transfer coefficient on the catalyst surface. Bottom right: Degree of mass transfer control for NO-, N₂O- and N₂ selectivity. For the analysis the temperature and NH₃ mass transfer coefficient at the front of the smooth single wire has been used.

The results show, that also the microstructure of the wire has an influence on the product selectivity. Even at the microscale, the catalyst performance is partly determined by the interaction of gas flow around the individually shaped cauliflower structures and surface chemistry and not fully determined by diffusion effects. As already pointed out by Wiser, this phenomenon goes beyond a simple increase in total surface area and a dilution of near-surface gas concentrations. From a modeling point of view, the picture gets even more complicated if one considers, that the reconstruction of the catalyst is a dynamic process. The catalyst shape changes throughout the campaign, beginning in the first hours of operation until the end of the campaign, when the gauzes become mechanically unstable and fragile. One possible option to tackle this problem, is to perform microscale CFD simulations to derive numerical adjustment factors that can then be used in larger gauze scale models with smooth wires. Therefore, one needs to perform an ensemble of simulations based on CT scans from different wire segments at different operation times. This requires a large number of expensive simulations, where the combined approach of simplified CFD calculation and degree of mass transfer control has a clear numerical advantage over the full CFD simulation.

6.5.5.2. Woven wire gauze study

In section 5.3.3 the effect of wire diameter and wire distancing on the N_2O selectivity has been studied for a two-dimensional single wire. The results revealed that with larger diameter and larger wire spacing, lower N_2O were obtained. The aim of this section is to investigate, if those correlations can be reproduced for simulations of more complex three-dimensional woven gauze catalysts. The results are then used to present a novel type of analysis for gauze catalysts, allowing to identify the contribution of each individual layer to the overall catalyst performance. A similar procedure was derived from Wiser to characterize Pt catalyst wires with a resolved microscale [132].

The structure of the catalyst investigated in this section is very similar to the woven gauze catalysts that are, to some extent, still in use for industrial operation. The geometry of the model and the computational domain are displayed in Figure 6.16. Simulations of woven gauzes with varying wire diameter d_w and mesh size D are conducted. An overview of all gauze types and their geometric parameters is given in Table 6.7.



Figure 6.16.: Geometry of the woven gauze catalyst. Left: Several layers of gauze catalyst inside the computational domain. At the contact points, the wires are connected by a pin-like segment with a diameter of $0.5d_{\rm w}$. This prevents single contact points and represents the merging due to the formation of cauliflower structures. Right: Side view (top) and frontal view (bottom) on the gauze configuration. Main flow is along the *z*-axis.

Similar to the simpler crossed wire configuration presented in previous chapter, the different gauzes are arranged in staggered configuration, i.e. each gauze is shifted by 0.5D horizontally (*x*-direction) as well as vertically (*y*-direction) with respect to the upstream gauze. To avoid single contact points and to account for the partial merging of the wires due to the formation of cauliflower structures, the wires are connected by a pin-shaped segment with an diameter of $0.5d_w$ at the contact points. Due to the staggered configuration, periodic boundary conditions are required at the external surfaces of the domain orthogonal to the direction of the main flow. As operating conditions, the standard conditions in Table 5.2 are used. To account for the surface chemistry, the kinetic model from Kraehnert was implemented. It was already shown that both mechanisms show a positive correlation between N₂O

selectivity and external mass transfer intensification, as well as catalyst temperature. Therefore, in terms of N_2O selectivity, the same qualitative results can be expected when using the kinetic model from Traversac.

#	Mesh density / cm^{-2}	$d_{ m w}$ / $\mu { m m}$	<i>D</i> / μm	No. of layers
1	1024	60	312.5	8
2	1024	90	312.5	8
3	1024	120	312.5	6
4	455	60	468.8	9
5	455	90	468.8	8
6	455	120	468.8	9
7	256	60	625.0	12
8	256	90	625.0	8
9	256	120	625.0	8

Table 6.7.: Geometric parameters of the different gauzes investigated in the CFD simulations: Mesh density,wire diameter d_w , mesh size D and number of gauze layers.



Figure 6.17.: Integral N₂O selectivity at the outlet of the reactor. Left: Temperature of the gauzes is solved during the simulations. Right: Gauze temperature fixed to T_s = 1100 K.

The integral N_2O selectivity at the reactor outlet as a function of wire diameter is presented in the left plot in Figure 6.17. For all mesh sizes, the N_2O selectivity decreases with increasing wire diameter. The results are in line with the investigations of the single wire and also the explanation follows the same rationale: For higher wire diameters the diffusion lengths and thus the mass transfer resistance increase. This leads to lower mass transfer rates and thus to a reduction in N_2O selectivity.

Comparing the different mesh sizes for a fixed wire diameter, the simulations predict a selectivity increase for lower mesh widths. This result is reasonable, as a rise in N_2O selectivity was also found for the single wire case when the wire spacing was decreased. Smaller mesh openings lead to a constriction and acceleration of the flow when passing through the mesh, thus increasing mass transfer and leading to higher N_2O selectivity. At the same time, the flow is also channeled towards the wires of the downstream gauze, that are oriented directly behind the mesh openings of the previous gauze, leading to a stagnation point of increased mass transfer and N_2O selectivity. The smaller the mesh size, the more the flow is

accelerated and the more pronounced the stagnation point. Discussing the effect of wire diameter, it should be mentioned that for a fixed mesh width, the confinement and the acceleration of the flow are more pronounced if the wire diameter is increased. The effect of increasing mass transfer resistance due to a larger diameter is thus superimposed by this acceleration effect. Figure 6.18 compares the distribution of local NH₃ mass transfer coefficient on the surface of the gauze catalyst for different wire diameters at a constant mesh size of $D = 468.8 \,\mu\text{m}$. The degree of mass transfer control for the N₂O selectivity is positive, thus the qualitative contours of local selectivity would resemble those of the local mass transfer coefficients in Figure 6.18.

The effects of increased diffusion lengths and flow confinement work in opposite directions. Since the fraction of surface elements with increased β_{NH_3} is higher for lower wire diameters, the effect of the shorter diffusion lengths seems to prevail the acceleration effect. This is confirmed by the negative slope of the integral selectivities in Figure 6.17.



Figure 6.18.: Local NH₃ mass transfer coefficient for different wire diameters. The results are compared for a constant mesh size of D = 468.8 µm.

The effect of an increased temperature of the first gauzes has not been considered in the discussion so far. Therefore, all simulations have been repeated, but this time the gauze temperature was fixed to $T_s = 1100$ K. The respective results are shown on the right side of Figure 6.17. Although, there is a general shift to higher selectivities, which is expected as the temperature is lower compared to the previous case, the trend in the results is conserved, i.e. larger wire diameters and mesh sizes lead to lower N₂O selectivities.

Although the contour plots in Figures 6.12 and 6.18 provide valuable information on the distribution and correlation of mass transfer intensity and product selectivity, it is hard to evaluate, how much different catalyst sections with certain mass transfer intensity contribute to the overall reaction. For a more quantitative analysis, the fraction of total conversion is plotted against the local NH_3 mass transfer coefficient for the first three layers of the gauzes, which is shown in Figure 6.19. Each bar represents the contribution of all surface elements with the same mass transfer coefficient to the integral conversion over the whole catalyst gauze.

For all gauze configurations, the highest mass transfer coefficients are found at the second gauze. This is in line with the preceding discussions and was explained by the channeling effect of the first gauze layer. The smallest mass transfer coefficients are obtained for the third gauze. This is expected, as the wires of the third gauze are not particularly exposed to the flow, since they are positioned in the flow shade of the first gauze. In all cases, the first gauze shows a maximum in fraction of total conversion.



Figure 6.19.: Fraction of total NH₃ conversion as a function of local NH₃ mass transfer coefficient.

This maximum corresponds to the frontal area of the wires, as mass transfer is highest there. When comparing the results at constant wire diameter, the profiles are shifted towards higher mass transfer coefficients for lower mesh sizes. This shift is also observed, when going from higher wire diameters to smaller ones, keeping the mesh size fixed. Both shifts are accompanied with an increase in N_2O selectivity.

This type of analysis allows to differentiate the contribution of each gauze to the total performance of the catalyst. It elucidates which layers are contributing most to unwanted N_2O formation and thus suggest, which gauze layers need to be optimized, either by changing the gauze geometry or its position relative to the other gauzes. An optimal gauze design would therefore aim for high fractions of total conversion at comparably low mass transfer coefficients for all gauzes, especially the second one.

6.5.6. Summary

In this section, a surface kinetic model for ammonia oxidation has been optimized and then expanded by equations accounting for external mass transfer and the resulting coupled system was analyzed with a degree of rate control analysis. It was found that the net rate of product formation is most sensitive to the mass transfer of the reactants, mostly NH_3 and O_2 , which is expected for a mass transfer limited reaction. The surface reactions showed significantly smaller sensitivities, with most of them exhibiting a X_{RC}^m close or equal to zero. In a next step, two computation strategies for X_{RC}^m have been presented and compared. The analytic approach using the Jacobian matrices of the system was found to outperform the numerical integration method by a speedup factor of almost 20. This advantage in performance is mostly due to the evaluation of the Jacobians beeing computationally far less expensive than the repeated numerical integration of the system of DAEs.

Different forms of degree of rate control analysis of the kinetic model were compared, where mass transfer was incorporated at different levels of detail. A $X_{\rm RC}$ analysis using the species bulk concentrations may lead to completely erroneous results in applications, where mass transfer limitations are present. The most advanced way to calculate the sensitivities is to use a reactor model, that implicitly accounts for species mass transfer by resolving the concentration gradients. Surprisingly, using only the kinetic model with mass transfer yields almost the same results for the sensitivities as with the full reactor-scale degree of rate control, but at only a fraction of the computational costs.

A novel approach for the characterization and development of structured catalysts has been presented. It combines flow simulations with the degree of mass transfer control analysis of a given surface kinetic model. The flow simulations require no implementation of the detailed kinetics and yield information on the distribution of local mass transfer intensity over the catalyst. The sensitivity analysis quantifies, how the changes in mass transfer govern the product selectivities. The usefulness of this tool was demonstrated by applying it to ammonia oxidation catalyst models of different complexity. In all cases, the combined approach and the CFD model with detailed kinetics yielded comparable results with respect to the effect of local mass transfer on product selectivity. This concept can also be used for investigations resolving the catalyst microscale. It was observed that a restructured Pt catalyst exhibit its N_2O selectivity maxima at the tip of the cauliflower-shaped structures, which protrude into the gas stream. This has been explained with the enhanced mass transfer rates at those points.

Finally, the effects of wire diameter and spacing on the N_2O selectivity were investigated for a threedimensional woven gauze. Results similar to the case of a single wire were observed. Furthermore, an alternative characterization method for the individual layers of a gauze with respect to their mass transfer characteristics was presented. Derived from this analysis, an optimized gauze layer design should aim for high fractions of total conversion at comparably low mass transfer coefficients.

6.6. Summation rule for degree of rate control

The concept of Campbell's degree of rate control $X_{\rm RC}$, which has been introduced in section 6.3.1, seems to be a conserved quantity: When summed over all individual elementary steps *i*, the $X_{\rm RC}$ for the net rate of species *j* is equal to unity as stated by equation (6.19).

Dumesic has proven this *summation rule* for a specific three-step reaction scheme, that leads to a single net reaction, making use of *De Donder* relations [150]. Jørgensen showed Equation (6.19) to hold true for a general multi-step surface reaction scheme with multiple pathways, leading to one net reaction, but assumed changes in surface coverages to be independent of changes in the rate constants [151]. However, the summation rule seems to hold true even for branched kinetic models that lead to several net reactions so that selectivities become an issue [116].

To the author's knowledge, the most general proof was given by Foley [148]. He showed that for an arbitrary function, the sum of sensitivities of that function with respect to its arguments is restricted to unity, due to the conservation of units.

In this work, a different strategy will be presented with which one can prove the validity of equation (6.19) for a general mean-field microkinetic model with an arbitrary number of net reactions. The proof proceeds by investigating a variant of the degree of rate control where, instead of a single rate parameter,

all rate parameters are varied simultaneously. In a first step it is shown that this *all parameter* degree of rate control is identical to the sum of the individual degrees of rate control. In a second step it is demonstrated that the *all parameter* degree of rate control is one for arbitrary microkinetic mechanisms.

6.6.1. Proof for an arbitrary microkinetic model

Mathematically, the *all parameter* degree of rate control of species $j X_{all,j}$, i.e. the simultaneous variation of all rate coefficients k_i , can be described as:

$$X_{\text{all},j} = \frac{1}{R_j} \lim_{h \to 0} \frac{\binom{k_1}{k_2}}{\binom{k_n - 1}{k_n R}} + h \cdot \binom{k_1}{k_2}}{\binom{k_1}{k_n R-1}} - R_j \binom{k_1}{k_2} \vdots \\ \binom{k_n - 1}{k_n R}}{\binom{k_n R-1}{k_n R}} = \frac{1}{R_j} \lim_{h \to 0} \frac{R_j (\mathbf{k} + h \cdot \mathbf{k}) - R_j (\mathbf{k})}{h}$$

$$(6.48)$$

where nR is the number of elementary reaction steps. From a mathematical point of view, the r.h.s. of Equation (6.48) defines a directional derivative. It can be seen from mathematical textbooks [152] that, if all partial derivatives of the net rates with respect to the rate constants are continuous, this directional derivative can be expressed as:

$$X_{\text{all},j} = \frac{1}{R_j} \nabla R_j(\boldsymbol{k}) \cdot \boldsymbol{k} = \sum_i \frac{k_i}{R_j} \left(\frac{\partial R_j}{\partial k_i}\right)_{k_l \neq i, K_i}$$
(6.49)

With Equation (6.49) it is shown that the *all parameter* degree of rate control is equal to the l.h.s. of Equation (6.19), which needs to be proven to be one. The remaining step is to show that X_{all} is one for arbitrary mechanisms. In a first step, it is demonstrated that the coverages θ of all surface species do not change, if all rate constants are multiplied by same the factor h simultaneously.

The net reaction rate of an reversible elementary step with index i is defined as:

$$r_i = k_i \prod_n \theta_n^{\nu_{in}} \prod_j c_j^{\nu_{ij}} - \frac{k_i}{K_{\text{eq},i}} \prod_n \theta_n^{\overline{\nu}_{in}} \prod_j c_j^{\overline{\nu}_{ij}}$$
(6.50)

 θ_n is the coverage of surface species n and c_j the concentration of gas species j. ν_{in} and ν_{ij} are the stochiometric coefficients in the forward reaction and $\overline{\nu}_{in}$ and $\overline{\nu}_{ij}$ the stochiometric coefficients in the reverse reaction of elementary step i. The rate constant of the reverse reaction can be expressed in terms of the equilibrium constant of the respective elementary step $K_{eq,i}$.

To simplify the later discussion, it should be noted at this point that increasing the rate constant by a constant factor h, the rate of step i increases by the same factor:

$$r_i(hk_i) = hr_i(k_i) \tag{6.51}$$

The steady state surface coverages for any set of rate constants **k** are determined by the solution of the following system of nonlinear algebraic equations (the gas species concentrations as well as the temperature are only parameters and kept constant):

$$\frac{\mathrm{d}\theta_n(\boldsymbol{k})}{\mathrm{d}t} = \sum_i \nu_{in} r_i(k_i) = 0$$
(6.52)

It is shown now that this solution $\theta_n(\mathbf{k})$ does not change, if the entire vector of rate constants \mathbf{k} is multiplied by a constant factor h, which is readily seen if Equation (6.51) is inserted into Equation (6.52):

$$\frac{\mathrm{d}\theta_n(h\mathbf{k})}{\mathrm{d}t} = \sum_i \nu_{in} r_i(hk_i) = h \sum_i \nu_{in} r_i(k_i) = 0$$
(6.53)

It is obvious that Equation (6.53) has the same solution as Equation (6.52), thus it is demonstrated that $\theta_n(h\mathbf{k}) = \theta_n(\mathbf{k})$. At this point it is emphasized, that surface coverages are independent of changes in \mathbf{k} only, if all rate constants are multiplied by the same factor h at the same time. If, for instance, only one rate constant is perturbed, as it is the case when evaluating $X_{\text{RC},ij}$, the solution of Equation (6.52) does change. As a consequence, the contribution of changes in the surface coverages to the numerical value of $X_{\text{RC},ij}$ cannot be neglected. This will be discussed in greater detail later, using the surface kinetic model introduced in 6.2.1 as an example.

The last step involves proofing that the all parameter degree of rate control is one, i.e. that

$$\frac{1}{R_j}\lim_{h\to 0}\frac{R_j(\boldsymbol{k}+h\cdot\boldsymbol{k})-R_j(\boldsymbol{k})}{h}=1$$
(6.54)

with the species net rates R_i being described by the following equation:

$$R_j = \sum_{i}^{nR} \nu_{ij} r_i \tag{6.55}$$

Using Equation (6.51), one obtains

$$R_j(\mathbf{k} + h \cdot \mathbf{k}) = R_j((1+h) \cdot \mathbf{k}) = \sum_i^{nR} \nu_{ij} r_i((1+h) \cdot k_i) = (1+h) \sum_i^{nR} \nu_{ij} r_i(k_i) = (1+h)R_j(\mathbf{k})$$
(6.56)

Inserting this result into Equation (6.54) yields

$$\frac{1}{R_j} \lim_{h \to 0} \frac{R_j(\mathbf{k} + h \cdot \mathbf{k}) - R_j(\mathbf{k})}{h} = \frac{1}{R_j} \lim_{h \to 0} \frac{(1+h)R_j(\mathbf{k}) - R_j(\mathbf{k})}{h}$$
$$= \frac{1}{R_j} \lim_{h \to 0} \frac{hR_j(\mathbf{k})}{h} = \frac{R_j}{R_j} = 1$$
(6.57)

With Equation (6.57) it was shown that the *all parameter* degree of rate control is equal to one for every species j, which according to the equality in Equation (6.49) must also hold true for the summation rule in Equation(6.19).

This summation rule has also a practical value: Most degree of rate control analyses, especially for microkinetic models involving a large number of elementary steps and species, require a numerical evaluation of the partial derivatives in equation (6.17). As $X_{\rm RC}$ turns out to be very sensitive to the accuracy of the numerical solution of the system of nonlinear algebraic equations in equation (6.52), the summation rule provides a fast and simple check criterion.

Now that a proof for the summation rule was given, the degree of rate control will be analyzed in greater detail. The species net rates R_j are a function of the rate coefficient vector k and surface coverages θ , which in turn depend on k. In order to describe the response of R_j with respect to changes in the rate coefficients, the chain rule needs to be applied. Equation (6.17) then yields:

$$\frac{k_i}{R_j} \left(\frac{\partial R_j}{\partial k_i}\right) = \frac{k_i}{R_j} \left(\frac{\partial R_j}{\partial k_i}\right)_{\theta} + \frac{k_i}{R_j} \sum_n \left(\frac{\partial R_j}{\partial \theta_n}\right)_k \left(\frac{\partial \theta_n}{\partial k_i}\right)_{\theta} = X_{\text{RC},ij}^k + X_{\text{RC},ij}^\theta$$
(6.58)

To keep notation lucid, the current indices are dropped and instead the superscript θ is used to denote that all surface coverages and all rate constants except k_i are fixed. The superscript k denotes that all rate constants and all surface coverages except θ_n are fixed.

 $X_{\text{RC},ij}$ is made up of two contributions: The first contribution $X_{\text{RC},ij}^k$ is the change in the net rate of gas species j with respect to the kinetic constant of elementary step i, keeping all surface coverages (and all k except k_i) fixed. The second term, $X_{\text{RC},ij}^{\theta}$, is the change in net rate of gas species j due to changes of the surface coverages that in turn are caused by the change in the rate constant of elementary step i.



Figure 6.20.: (a) Degree of rate control analysis for N₂O. (b) degree of rate control analysis for N₂O with the two terms contributing to $X_{\rm RC}$ according to Equation (6.58). In both cases only elementary reactions with a significant $X_{\rm RC}$ are shown here.

Figure 6.20a shows the $X_{\rm RC}$ for N₂O using the microkinetic model from Traversac (see section 6.2.1). In Figure 6.20b the degree of rate control is split up into the two contributions according to Equation (6.58). The $X_{\rm RC}$ for all elementary steps can be found in Table D.1 in the appendix.

For all elementary steps, $X_{\rm RC}$ is determined by the contribution due to the changes in surfaces coverages $X_{\rm RC}^{\theta}$, except for the elementary step describing the production/consumption of the very species, R22 in the case of N₂O. $X_{\rm RC}^k$ only has a contribution for elementary steps, which directly lead to the production or consumption of species j. The explanation for this is rather simple: The sum in Equation (6.55) only contains the elementary steps producing or consuming species j, as the derivative of R_j with respect to k_i is zero for all other steps. This example demonstrates, that the changes of the surface coverages with respect to the rate constants cannot be neglected. This has another interesting consequence: When summed over all elementary steps, the contribution of the surface coverage terms $(X_{\rm RC,ij}^{\theta})$ add up to zero. This means that the second contribution $(X_{\rm RC,ij}^k)$ adds up to one, which is in accordance to the summation law in Equation (6.19).

6.6.2. Proof for an arbitrary microkinetic model with external mass transfer

Finally, the proof of the summation rule is extended to a degree of rate control analysis of an arbitrary microkinetic model with mass transfer (see section 6.3.2). The steady state surface coverages are now a function of rate constants and mass transfer coefficients. Thus, the contributions of the degree of rate control arising from the perturbation of the mass transfer coefficients have to be included into the sum in order for it to be equal one, as described in (6.26). It is straighforward to realize, that the parameter vector \mathbf{k} , in addition to the rate constants, now also contains the mass transfer coefficients of all gaseous species in the system:

$$\boldsymbol{k} = \begin{pmatrix} k_1 \\ \vdots \\ k_{nR} \\ \beta_1 \\ \vdots \\ \beta_{nG} \end{pmatrix}$$
(6.59)

Here nG is the number of gas species in the system. From Equation (6.49) it can be demonstrated quite easily, that the *all parameter* degree of rate control with mass transfer of species j, $X_{\text{all},j}^m$ is still equal to the sum over the degree of rate control with mass transfer of species j with respect to the elementary steps.

Again, all that is left to do is to show that $X_{\text{all},j}^m$ is equal to one. Including mass transfer, the steady state surface coverages θ and near-surface concentrations c_s for any set of rate coefficients and mass transfer coefficients k is now given by the solution of the following system of nonlinear algebraic equations:

$$J_{j}(\boldsymbol{k}) - R_{j}(\boldsymbol{k}) = \beta_{j}(c_{\mathrm{b},j} - c_{\mathrm{s},j}) - \sum_{i} \nu_{ij} r_{i}(k_{i}) = 0$$

$$\frac{\mathrm{d}\theta_{n}(\boldsymbol{k})}{\mathrm{d}t} = \sum_{i} \nu_{in} r_{i}(k_{i}) = 0$$
(6.60)

Using Equation (6.51) it can again be shown that the solution of Equation (6.60) does not change, if the whole parameter vector k is multiplied by a constant factor h:

$$J_{j}(h\mathbf{k}) - R_{j}(h\mathbf{k}) = h\beta_{j}(c_{\mathrm{b},j} - c_{\mathrm{s},j}) - \sum_{i} \nu_{ij} r_{i}(hk_{i}) = h\beta_{j}(c_{\mathrm{b},j} - c_{\mathrm{s},j}) - h\sum_{i} \nu_{ij} r_{i}(k_{i}) = 0$$

$$\frac{\mathrm{d}\theta_{n}(h\mathbf{k})}{\mathrm{d}t} = \sum_{i} \nu_{in} r_{i}(hk_{i}) = h\sum_{i} \nu_{in} r_{i}(k_{i}) = 0$$
(6.61)

The factor *h* in Equation (6.61) can be eliminated, which leads to the same expression as in Equation (6.60). Thus, both set of equations must have the same solution, i.e. it was demonstrated that $\theta_n(h\mathbf{k}) = \theta_n(\mathbf{k})$ and $c_{s,j}(h\mathbf{k}) = c_{s,j}(\mathbf{k})$. From this point, the proof proceeds identical to the case without mass transfer, starting from Equation (6.54).

6.6.3. Summary

A mathematical proof for the summation rule of the degree of rate control was given. This was done introducing the concept of a *all parameter* degree of rate control and using its property of defining a

directional derivative that is equal to the sum over the degree of rate control of all individual elementary steps. The proof is valid for an arbitrary surface kinetic model. Including the species mass transfer coefficients into the parameter vector k and following the same strategy, the proof of the summation rule was extended to the degree of rate control of a surface kinetic model with coupled mass transfer.

6.7. Conclusion

Industrial ammonia oxidation is just one prominent example for a number of large scale industrial processes carried out at high temperatures and short contact times, in which the overall reaction is controlled by external mass transfer. In this chapter, two- and three-dimensional simulations of reactive flow over Pt catalyst gauzes have been combined with sensitivity analysis of a chemical reaction network in order to further quantify the effect local mass transfer on product selectivity.

The investigations have shown, that for a correct degree of rate control analysis of surface kinetics under mass transfer limitation, the network of elementary reactions has to be extended by equations accounting for the mass transfer of species from the gas phase to the catalyst surface. Neglecting these mass transfer effects can lead to severe errors in the prediction of sensitivities. It was furthermore demonstrated that X_{SC}^m can be calculated from the DAE system, describing the mass transfer coupled surface chemistry, with almost the same accuracy as from a full CFD reactor model, but at a fraction of the numerical effort. This numerical advantage can be even further increased if sensitivities are calculated from the Jacobians of the chemical rates instead from the consecutive numerical integration of the system of DAEs. For the kinetic model presented in this chapter, a speed up factor of almost 20 was observed when using the Jacobians for the evaluation of X_{RC}^m .

The effect of variations in local mass transfer on the product selectivity can be quantitatively described by $X_{SC,\beta}^m$, i.e. the sensitivity of ta product species selectivity with respect to the overall mass transfer intensity. This sensitivity measure, called *degree of mass transfer control*, represents a more direct link between local mass transfer intensities and product selectivity compared to the selectivity orders n_{S_j} presented in chapter 5. This is because, in addition to the selectivity orders, $X_{SC,\beta}^m$ implicitly contains the information on how mass transfer intensity affects the near-surface NH₃ concentration. Thus, it is not surprising that a positive $X_{SC,\beta}^m$ is found to result in an increase in N₂O and N₂ selectivity.

Combined with simulations of flow over structured catalysts, $X_{SC,\beta}^m$ represents a novel and useful tool for the investigation of gauze catalyst geometries: The flow simulations are used to obtain the distribution of local mass transfer coefficients along the surface of the catalyst. These simulations do not need to contain a full description of the surface chemistry. Assuming external mass transfer limitations to be present, a global fast first-order reaction with respect to the limiting reacting species or a Dirichlet-type boundary condition on the catalyst surface ($c_{s,i} = 0$) is sufficient. The degree of mass transfer control then yields information on how this change in local mass transfer intensity translates into changes in the selectivity towards the products. The application of such an decoupled approach over the full CFD reactor simulation is clearly motivated by its reduced numerical effort. In most cases the numerical integration of the chemical rate equations is the most time consuming and thus rate-limiting step during a full reactor simulation. Furthermore, the decoupling of flow simulation and chemistry allows for more flexibility. The surface kinetic model under investigation can be exchanged or parameters be adjusted without the necessity to rerun the expensive CFD model. All that is required is a degree of mass transfer control analysis with the new kinetic model or set of parameters, which in most cases is a matter of seconds, especially when using the the analytic evaluation of partial derivatives described in this chapter.

Ammonia oxidation catalysts of different geometric complexity have been investigated using the

combined approach of flow simulation and degree of mass transfer control. Due to a positive X_{SC,β,N_2O}^m and X_{SC,β,N_2}^m , for catalyst surface elements with high mass transfer coefficients, a higher N₂O and N₂ selectivity was predicted, which was confirmed when comparing the results to CFD calculations including the full mechanistic model.

Using a catalyst model derived from μ CT images of a restructured Pt wire, it was demonstrated that this tool can yield valuable insight also at the microscale of the catalyst. Areas of high mass transfer intensity could be located at the tips of the outgrowing cauliflower shaped structures, that were exposed to the gas stream. Due to their positive degree of mass transfer control, higher N₂O and N₂ selectivities were predicted at those areas of the catalyst. This result was also confirmed by the full CFD simulation.

Reactive flow simulations of three-dimensional woven gauzes have been conducted. The basic trends concerning the influence of wire diameter and wire distance on the N_2O selectivity, that were observed for the two-dimensional catalytic cylinders, were also observed for this kind of gauze geometries. Different layers of a catalyst gauze package have been investigated with respect to their mass transfer characteristics by means of a statistical analysis. Improved performance, i.e. lower N_2O selectivity, was observed, when a gauze segment exhibited high overall conversion at comparably low mass transfer coefficients. This is in line with the suggestion made in the previous chapter, that the design of future gauze catalysts should focus on minimizing the mass transfer intensities on the wires in order to minimize the production of N_2O and N_2 .

It was demonstrated that such kind of tools and statistical analyses show great potential to assist rational catalyst design and the search for improved gauze shapes. Their application is of course not limited to Pt gauze catalysts for industrial ammonia oxidation. In principle, they can be employed for any heterogeneously catalyzed reaction, where the overall rate is limited by the transfer of reactants to the catalyst surface and the selectivities to the different products become a function of the catalysts geometry.

Finally, it was proven for an arbitrary surface kinetic model, that the sum of the sensitivities of a degree of rate control analysis is a conserved quantity equal to unity. It was shown, that this *summation rule* also applies, when the chemical mechanism is extended by equations describing species mass transfer in terms of mass transfer coefficients. The summation rule constitutes a useful criterion to check the convergence of a degree of rate control analysis, since the chemical rates need to be determined with high accuracy due to the small changes in the parameters.

7. The effect of upstream turbulence on the surface chemistry

7.1. Introduction

Industrial ammonia oxidation is carried out in large burning vessels reaching several meters in diameter. Using the reactor diameter as a characteristic length L in Equation (3.31), Reynolds numbers Re in the order of 10^5 are expected at the reactor scale. Thus, the flow upstream of the Pt/Rh catalyst gauzes is expected to be turbulent. The effect of turbulent flow on the surface chemistry has for the most part been neglected in the investigation, modeling and discussion of ammonia oxidation reactors so far. This is mainly contributed to the assumption of a laminarized flow throughout the gauze catalyst, which is often made by researchers. This is reasoned with low Re in the order of 10^{-4} m. Although this may be a good assumption for deeper sections of the gauze pack, it has not yet been clarified how turbulent flow interacts with the top layers of catalyst gauze and influences its performance. This question is of further significance, as most of the ammonia is converted at the first gauze layers.

A general assumption that is often made when using detailed surface kinetics in reactor simulations states that the rates of chemical reactions on the catalyst surface occur on a much shorter timescale than characteristic variations in the species' concentrations and temperature of the surrounding fluid. Thus, the surface coverages can be assumed to be in quasi-steady state [153]. In highly turbulent flow, fluctuations in velocity-, concentration- and temperature field can also occur on relatively small time and length scales. In this case, the assumption of a quasi-steady state for the surface chemistry may not longer hold, depending on the difference in timescale for the chemical kinetics and turbulent fluctuations. If the overall reaction is limited by external mass transfer, the time required for the surface coverages to reach steady state is also controlled by the transport of species through the concentration boundary layer to the catalyst surface.

In the previous chapters, it was demonstrated that under industrial conditions the selectivity of the ammonia oxidation reaction is influenced by the mass transfer intensity throughout the catalyst, which in turn is determined by the interaction of the steady state flow field with the catalyst geometry. If the flow contains turbulent structures, mass transfer intensity also becomes a function of time. In general, turbulent effects increase heat and mass transfer due to enhance mixing of the flow [42]. This raises the question, if and to what extent turbulent flow influences mass transfer and thus the selectivity of the process. This is not only interesting for plant operators and plant manufacturers, but also from the modeling point of view, since it helps to asses whether turbulent effects need to be considered in gauze scale simulations or if they can be neglected.

In the following chapter, a first attempt to study the effect of upstream turbulence on the performance of the ammonia oxidation catalyst will be presented. Large eddy simulations are carried out for an isolated single wire as well as for a configuration of multiple wires in cross flow assuming a fast first-order reaction for NH_3 consumption at the catalyst surface. The solution of a detailed surface kinetic model is performed in a post-processing step using NH_3 mass transfer coefficients which are extracted from

the simulation of the turbulent flow. The detailed chemistry is described using the mechanistic model published by Kraehnert [80], which was presented in section 5.2.1.

The investigations start with an isolated single wire. The effect of transient local mass transfer on the N_2O selectivity around the catalytic wire is studied. Conversion-weighted time averages of selectivity are compared to the selectivity obtained from a wire in laminar cross flow. It is furthermore investigated if the mass transfer controlled surface reaction is fast enough to follow the fluctuations in external mass transfer intensity induced by the turbulent flow field.

The study of the effect of turbulence-induced fluctuations in local mass transfer on the N_2O selectivity is then extended to a multi-wire configuration, consisting of several rows of wires with a wire spacing equal to the typical mesh size of woven gauzes.

7.2. Computational model

A description of the LES model for the single wire and multiple wire configuration is given in the following section. Furthermore, the details for the coupling of the surface chemistry with the flow simulation are presented. As for the previous investigations, the wire diameter is set to $d_w = 100 \mu m$. The computational domain for the single wire case consists of a 4 mm (= $40d_w$) long wire segment, running in *z*-direction, which is placed inside a box with dimensions of $80d_w \times 80d_w \times 40d_w$. The distance from the wire center to the inlet face of the domain measures $30d_w$, with the main flow being in *x*-direction. The domain was discretized into 2.8 million elements.

7.2.1. CFD model

Figures 7.1 and 7.2 contain details about the geometry and the computational mesh of the single wire and the multi-wire case.



Figure 7.1.: Geometry of the single wire and the computational domain, as well as the computational mesh around the wire. The wire diameter is set to $d_w = 100 \mu m$. The domain spans $80d_w$ in x-, $80d_w$ in y- and $40d_w$ in the *z*-dimension with the main flow being in *x*-direction. The wire is positioned $30d_w$ downstream relative to the inlet of the domain.



Figure 7.2.: Geometry of the multi-wire setup and the computational domain, as well as the computational mesh around the wires. The wire diameter is set to $d_w = 100 \ \mu\text{m}$. The domain spans $60d_w$ in x-, $20d_w$ in y- and $20d_w$ in z-dimension with the main flow being in x-direction. The catalyst is represented as three rows of parallel wires in staggered configuration.

The multi-wire case consists of three rows of parallel wires, stretching 2 mm in *z*-direction, arranged in staggered configuration. Wire and row spacing is identical to the two-dimensional 10-wire case, i.e. a center-to-center distance between two neighboring wires in a row measures $3d_w$ and the individual rows are shifted by $2d_w$ in *x*-direction which the direction of the main flow. Each row contains 7 wires confined inside a computational domain with dimensions of $60d_w \times 20d_w \times 20d_w$. The domain was discretized into five million elements.

During the LES, the balance equations for mass, momentum, energy and species, as well as the dynamic kinetic energy subgrid-scale model are solved (see section 3.4.2). The boundary conditions applied in the simulations are equal for both models. At the inlet of the domain the *Spectral Synthesizer* method, as implemented in ANSYS Fluent [53], is used for the synthetic generation of turbulence at the boundary.

A mean velocity of $u_{\rm m} = 0.75 \text{ m s}^{-1}$, a turbulent intensity $I_{\rm t}$ of 80% and a turbulent viscosity ratio $(\mu_{\rm t}/\mu)$ of 40 are used to parametrize the turbulence generator. Due to the comparably high value for the turbulent intensity, the generated results are used to assess the maximum effect of the upstream turbulence. With a first reactor-scale LES, values of $I_{\rm t}$ around 30% were obtained for a fully developed turbulent flow upstream of the catalyst gauzes [154]. A pressure outlet is chosen at the domain exit. Periodic boundary conditions are implemented on the remaining 4 faces and the temperature of the catalyst wires was fixed to 1100 K in all simulations.

Due to periodic boundary conditions, the dimensions of the model (in y- and z-direction) need to be chosen sufficiently large. For the single wire case this ensures that the flow field around the wire is not influenced by the wire next to it.

All other operating conditions are equal to the standard conditions in Table 5.2. The complex surface

chemistry is replaced by a fast global reaction in which ammonia near the catalyst surface is entirely converted to NO (R1), i.e. selectivity is not accounted for. The respective reaction rate is a first order with respect to the ammonia concentration:

$$R = k c_{\rm NH_3} \tag{7.1}$$

The rate constant k is chosen to be $k = 100 \text{ m s}^{-1}$, a value high enough to ensure a fast reaction and thus mass transfer limitation. A time step of $\Delta t_{\text{LES}} = 10^{-6}$ s has been chosen in order to obtain a CFL number below 1 at any time (see Equation (7.2)). The LES was initialized using the solution of a converged RANS (k- ω -SST) simulation. After initialization, the model was equilibrated by running the simulation for three domain residence times before data recording was started. During the simulation, local mass transfer coefficients along the surface of the wires are recorded as a function of time. The data was logged for every 20th time step ($\Delta t = 2 \cdot 10^{-5}$ s) at $z = 20d_w$ for the single wire and at $z = 10d_w$ for the multi-wire case.

7.2.2. Coupling of LES with surface chemistry

The simultaneous solution of the conservation equations and surface chemistry is a numerically challenging task, even with modern CFD codes. This is especially true for LES, where the computational mesh needs to be sufficiently fine to resolve larger eddies above a certain size (implicitly defined by the mesh size), which contain most of the kinetic energy. To obtain representative results, in a LES typically more than 75% of the total kinetic energy need to be resolved [155]. Furthermore, in most cases mesh size and time step are related and cannot be chosen independently from each other. In transient flow simulations, smaller mesh sizes generally require smaller time steps for a solution to be stable. This stability criterion is expressed in terms of the Courant-Friedrich-Lewy number (CFL), which should be below 1.

$$CFL = \frac{u_i \,\Delta t_{LES}}{\Delta x_i} \tag{7.2}$$

where u_i is the velocity component in the *i*th spatial direction, Δt_{LES} is the time step and Δx_i is the size of a mesh element in the the *i*th direction. If the description of detailed chemistry is integrated in flow simulations, the chemistry ODE solver needs to be called a large number of times. This can slow down the simulation significantly, especially if large chemical mechanisms are implemented, which often tend to be stiff. If the overall reaction is controlled by external mass transfer, one possible approach to surpass this problem is running the simulation in a two-step process. This involves decoupling the LES from the solution of the surface chemistry and solving the chemical kinetics with coupled mass transfer in a post-processing step.

The LES of the resolved catalyst allows to extract time-resolved local NH_3 mass transfer coefficients from the simulation. The mass transfer coefficients can be calculated using Equation (6.42). In the next step, the extracted mass transfer coefficients are used for a time integration of the surface kinetic model (from Kraehnert) with coupled mass transfer. This involves the solution of Equations (6.15) and (6.16) and will be called *0-dimensional model*. The integration procedure proceeds via the following scheme:

1. A steady state solution of the DAE system is generated for the first mass transfer coefficient of the data set at $t_0 = 0$ s, yielding a set of surface coverages θ_0 and near-surface concentrations and $c_{s,0}$.

- 2. Starting with θ_0 and $c_{s,0}$ as initial conditions, the system is integrated in time until $t_1 = \Delta t$, using the next mass transfer coefficient of the data set at t_1 . Note that Δt is not necessarily equal to the internal time step of the LES but to the time interval with which the data was recorded.
- 3. Starting from the solution of the previous time step t_{i-1} (θ_{i-1} and $c_{s,i-1}$), the DAE system is further integrated until $t_i = t_{i-1} + \Delta t$, using the mass transfer coefficient at t_i to obtain the solution θ_{t_i} and c_{s,t_i}
- 4. Step 3 is repeated until the final integration time t_{end} is reached.

If data sampling from the LES is performed for a sufficiently long time, average values for product selectivities can be calculated.

7.3. Results

The performance of catalytic wires for ammonia oxidation in turbulent cross flow has been studied and the results are presented in the following sections. In the first part, the approach of decoupling fluid flow and surface chemistry will be validated. The main part is dedicated to answer the question, if upstream turbulence may affect the N_2O selectivity to a significant extent, and whether further studies need to consider these turbulent effects or if the assumption of laminar flow throughout the whole catalyst gauze is sufficient. This is done by studying an isolated catalyst wire first and then extending the investigations to a more complex configuration of multiple wires.

7.3.1. Validation of chemistry coupling

In a first step it is demonstrated that the simplified approach in which the solution of the surface chemistry is decoupled from the flow simulation yields similar results as the CFD model with implemented detailed kinetics. As a test case, the two-dimensional 10-wire model is utilized.

In the simplified approach, a steady state solution of the CFD model using a fast global reaction is generated. As described in section 7.2.2, mass transfer coefficients are extracted along the surface of the wires and the 0-dimensional model of kinetics with mass transfer is solved yielding the chemical species rates. The obtained rates for NH_3 consumption and N_2O production are compared to the steady state rates from the CFD model with detailed kinetics in parity plots shown in Figure 7.3. For better visualization, the rates at each wire are scaled with the respective maximum rate from the full CFD model. For both species the rates predicted by the two models agree well for the first wires. Only from the fifth wire on, the relative rates start to drift away from the parity line noticeably, with the simplified approach more and more underestimating the rates. However, as it was demonstrated in earlier chapters, conversion is almost complete after the first three wires, thus the errors induced at the rear wires do not significantly contribute to the integral result. This is further confirmed by the results in Table 7.1, which contains the conversion weighted average of the relative error in N_2O selectivity, as well as the average NH_3 consumption rate over each individual wire.

As depicted in the parity plots, the deviation at the first wires is small and constantly increases towards the rear of the catalyst. The growing error arises from the fact that when solving the kinetic model with mass transfer, the species concentrations at the reactor inlet are used as bulk concentrations for the calculation of the species fluxes according to Equation (6.12). This assumption becomes more inaccurate for the rear wires, as the composition changes throughout the catalyst.

The average NH₃ rate on the other hand decreases exponentially, reducing roughly by a factor of two from wire to wire. As the rate of ammonia conversion declines faster than the relative error increases,



Figure 7.3.: Scaled NH₃ consumption (red) and N₂O production (blue) rates at the wire surface obtained with the 0-dimensional model versus the respective rates predicted by the full CFD model. The rates at each wire are scaled with the maximum rate predicted by the CFD model. The dotted line represents the parity line with a slope of 1.

the high errors at the rear wires do not significantly contribute to the overall result, thus ending up with a good agreement between the simplified apporach and the full CFD model.

Wire no.	rel. error $S_{ m N_2O}$ / %	$\overline{R}_{ m NH_3}$ / mol m ⁻² s ⁻¹
1	0.4	3.81
2	0.7	3.12
3	1.3	1.64
4	2.6	0.83
5	4.3	0.41
6	6.3	0.20
7	8.4	0.10
8	10.6	0.05
9	12.6	0.02
10	14.6	0.01

Table 7.1.: Conversion weighted relative error of N₂O selectivity and average rate of NH₃ consumption over the individual wires.

7.3.2. Single wire

In this section the results for the isolated single wire catalyst are presented. The flow field upstream and downstream of the wire is investigated. Then the time-averaged temperature and concentration fields will be compared to those obtained from a steady state laminar flow. This is followed by an analysis of local mass transfer and the N_2O selectivity around the wire. Finally, the response of the surface kinetic model to artificial changes in mass transfer intensity is studied.

7.3.2.1. Flow regime

To get a first insight on the behavior of the flow field around the wire, the flow velocity at certain distances relative to the single wire was recorded during the LES. Figure 7.4 shows the velocity magnitude as a function of time (a) $1d_w$, (b) $2d_w$ and (c) $15d_w$ upstream, as well as (d) $1d_w$ downstream of the catalyst surface. When examining the profiles in plots (a) to (c), it is relatively easy to see that the velocity fluctuations increase with increasing distance from the wire. The root-mean-square-error (RMSE) of the velocity magnitude puts this into a more quantitative statement, as it is a direct measure of velocity fluctuations and thus turbulent kinetic energy. This decline in velocity fluctuations is the result of the laminarizing effect of viscous boundary layer around the hot wire. Furthermore, the flow heats up when it approaches the wire, increasing the fluids viscosity and thus enhancing flow laminarization.

The smallest absolute fluctuations and thus the lowest RMSE are observed at the position $1d_w$ behind the wire at position (d). This is expected, since this point lies in the flow shade of the wire and is thus shielded from larger eddies, which either are moving around the wire or have dissipated at the wire. Interestingly, although at this position the RMSE is small compared to the upstream positions, a broader spectrum of fluctuation frequencies are observed. This is most likely due to mostly smaller sized eddies being present in the wake of the cylinder.

Additional information about the flow can be obtained from the power spectral density (PSD) of the velocity fluctuations $u - u_m$, where u is the instantaneous velocity and u_m the time-averaged velocity at the respective positions. This gives the spectrum of the turbulence kinetic energy in the frequency domain. Such a spectrum is shown in Figure 7.5 for the 4 different positions. In all spectra, no energy gap is observable and a smooth transition from larger eddies (lower frequencies) to smaller eddies (higher frequencies) is obtained. This smooth vortex cascade is typical for turbulent flows, where the kinetic energy is transferred from large vortices, containing most of the kinetic energy, to small vortices



Figure 7.4.: Velocity magnitude and root-mean-square-error of the velocity magnitude at several distances from the single wire. (a) 1 wire diameter upstream, (b) 2 wire diameters upstream, (c) 15 wire diameters upstream and (d) 1 wire diameter downstream of the wire. Average inlet velocity is 0.75 m s^{-text1}.

with low energy content [52]. At a frequency of around $4 \cdot 10^3$ Hz the spectra exhibit a bend, which correspond to the limiting frequency determined by the size of the computational grid according to $f_{\rm crit} = u_{\rm m}/4\Delta x$, with Δx being the size of the grid elements. Below this threshold, the grid is not able to resolve eddies of smaller frequency accurately, due to numerical dispersion caused by the numerical scheme [155]. Note that for higher distances to the wire, this threshold frequency is slightly shifted towards lower frequencies as the grid in the free stream becomes coarser. According to [155], for a reliable LES solution, the ratio of the energy content of the dominating (large scale) structures and the energy content of the structures at $f_{\rm crit}$ should be at least one order of magnitude. In the present simulation, this range spans at least 5 orders of magnitude which is a satisfying result. In total, almost the entire kinetic energy is resolved and only a small part is modeled within the subgrid-scale model.



Figure 7.5.: Power spectral density recorded at certain distances from the wire: (a) one wire diameter upstream, (b) two wire diameters upstream, (c) 15 wire diameter upstream and (d) one wire diameter downstream of the single wire. A sample time of 240 ms and a sampling frequency of 250 kHz was used.

7.3.2.2. Temperature and concentration field

Figures 7.6 shows the temperature- and NH₃ moles fraction profiles at the plane at $z = 20d_w$. In case of the LES, an instantaneous snapshot at t = 30 ms, as well as a time average over 100 ms is shown. For the purpose of comparison, the respective contours obtained from a steady state laminar simulation is also included. In all cases the temperature of the wire was fixed to $T_s = 1100$ K.

As expected, in all cases mass and heat transfer limitations are observed indicated by strong gradients around the wire. For the instantaneous LES time frame, non-symmetric and chaotic temperature and concentration profiles are obtained, as expected for turbulent flow with transient fluctuations of the velocity field around the wire. Comparing the time-averaged temperature and mole fraction field from the LES to the laminar case, a considerably more compact profile in the wake of the wire is observed for the LES. Here, significantly thinner temperature and concentration boundary layers indicate an enhanced mixing due to the turbulent flow, leading to increased heat and mass transfer.



Figure 7.6.: Temperature (top row) and NH₃ mole fraction (bottom row) obtained from (a) a laminar steady state simulation, (b) the time-averaged LES and (c) an snapshot of the LES.

7.3.2.3. Mass transfer

Figure 7.7 displays the local Sherwood number (*Sh*) along the surface of the wire at a height of $z = 20d_w$ (half the wire length in the domain) for different points in time. In addition to the local variation of mass transfer, due to the fluctuation of the flow field, also a strong variation in time can be observed. In contrast to the results for the laminar two-dimensional single wire, the maximum and minimum *Sh* are not necessarily found at the front and rear side of the wire, depending on the instantaneous configuration of the flow around the wire. As an example, at 1 ms the highest mass transfer intensity is found at an angle of about 30 degrees, indicating that in this time frame the wire is attacked by the flow in a slightly skewed angle compared to the main flow direction.

Figure 7.8a displays the local *Sh* as a function of time at three different positions on the catalyst wire, i.e. at the stagnation point on the front side ("Front"), at the tip of the wire at 90 degrees ("Top") and at the rear side at 180 degrees ("After") at a height of $z = 20d_w$. *Sh* is calculated via the following equation:

$$Sh = \frac{\beta_{\rm NH_3} \, d_{\rm w}}{D_{\rm NH_3}} = \frac{J_{\rm NH_3} \, d_{\rm w}}{D_{\rm NH_3} \, \left(c_{\rm b, NH_3} - c_{\rm s, NH_3}\right)} \tag{7.3}$$

where $J_{\rm NH_3}$ is the net molar flux of ammonia to the catalyst surface. Due to the fluctuations of the



Figure 7.7.: Sherwood number from the LES plotted along the perimeter of the single wire for different points in time.



Figure 7.8.: (a) Sherwood number extracted from the LES and (b) N₂O selectivity calculated with the 0dimensional model as a function of time at three different positions around the wire surface: front side (red), on top of the wire (red) and at the rear side (blue).

velocity field around the wire, the local Sh also shows large variations in time. These variations are declining when moving from the "Front" over the "Top" to the "After" position, which is expected, as the wire front is more exposed to the eddies than the back side of the wire.

The N₂O selectivity obtained from the 0-dimensional model using the respective *Sh* extracted from the LES are shown in Figure 7.8b. Interestingly, the time profiles of *Sh* and S_{N_2O} look almost identical. This indicates that surface kinetics are fast enough to follow the fluctuations in local mass transfer intensity induced by the turbulent flow field. In other words, the chemical system is in quasi-steady state at every time. To validate this preliminary assumption, the calculated selectivity at every time frame is compared to the case of an infinite fast surface chemistry. This is equivalent to calculating the steady state solution of Equations (6.15) and (6.16) for every *Sh* at every point in time. Weighted with the local and momentary NH₃ consumption rate, and averaged over all wire positions and time frames, the RMSE of the N₂O selectivity only accounts to 0.00024%, thus confirming the chemical system being in quasi-steady state at all times.

7.3.2.4. Influence on N₂O selectivity

The time-averaged local Sherwood number obtained from the LES is plotted against the perimeter of the single wire in Figure 7.9a together with Sh from the steady state laminar flow. Again, the values are extracted at a height of $z = 20d_w$. Qualitatively, the curve for the time-averaged Sh matches the one obtained for the laminar flow, with a maximum in mass transfer intensity at the stagnation point of the wire and a minimum at the rear side of the wire. In case of the LES, at the wire front the effect of the velocity fluctuations on the mass transfer intensity is more or less averaged out, as Sh is close to those obtained with laminar flow. At larger angles the deviation between the two models increases. The eddies in the turbulent flow attack the wire at different angles and the minimum in mass transfer is not observed at an angle of 180 degrees at all times. Thus on average a higher Sh is observed in the rear part of the wire compared to the laminar case. Looking at the steady state laminar and the time-averaged NH₃ mole fraction profiles in Figure 7.6a and Figure 7.6b, the boundary layer thicknesses at the stagnation point of the wire are almost equal. At the rear part, however, a much thinner boundary layer is observed for the LES, thus explaining the increased average mass transfer intensity.



Figure 7.9.: Comparison of (a) Sh and (b) N₂O selectivity along the wire perimeter for laminar flow (black) and the time-averaged LES (blue). Note that in the case of the LES, the averaged Sh in (a) is the arithemic mean over all time points while for the calculation of the N₂O selectivity in (b) the selectivity at each time frame is weighted with the respective consumption rate of ammonia according to Equation (7.4). The orange curve in (b) corresponds to the N₂O selectivity calculated using the time-averaged Sh from the LES shown in (a).

The resulting N_2O selectivities for the two models along the wire circumference are plotted in Figure 7.9b. For the calculation of the LES time average, the N_2O selectivities are weighted with the respective NH_3 consumption rate, according to the following equation:

$$S_{N_2O} = \frac{\sum_{i} S_{N_2O,i} R_{NH_3,i}}{\sum_{i} R_{NH_3,i}}$$
(7.4)

The index *i* runs over all time points. This takes into account, that for higher Sh a surface element exhibits a higher differential conversion proportional to the consumption rate of NH₃ and thus the respective differential N₂O selectivity needs to be weighted accordingly.

As expected, due to the positive $X_{SC,\beta}^m$ for N₂O, the averaged N₂O selectivity obtained with the LES is higher than for the laminar case at all positions on the wire surface. The selectivity obtained for

the time averaged Sh from the LES of Figure 7.9a is observed to be lower than the average selectivity calculated via Equation (7.4). This indicates, that non-weighted time averages for Sherwood numbers or mass transfer coefficients may not be suitable to properly determine integral selectivities.

The integral results over the whole wire can be obtained by averaging the selectivities over all wire position (at the height of $z = 20d_w$), again weighted with the respective rate of ammonia consumption. In case of the LES, the index *i* in Equation (7.4) now runs over all time frames and all discretized surface elements of the wire. The results are summarized in Table 7.2.

Table 7.2.: Integral selectivities over the single wire obtained for from the laminar simulation and the LES.

Flow model	$S_{ m N_2O}^{ m I}$ / %
Laminar	1.60
LES average	1.70

Similar integral selectivities are obtained for the LES and the laminar flow, with a deviation of only 0.1%. Although the difference in selectivity is more pronounced in the back of the wire (about 0.2% absolute), the rear of the wire does not contribute as much to the integral selectivies as the areas at the front, due to the lower reaction rates. Even though there are large fluctuations in *Sh*, the average *Sh* of the turbulent flow is predicted to increase only slightly compared to the case of laminar flow. This observation, in combination with the fast surface chemistry results in a weakly pronounced influence of the turbulent upstream flow on the N₂O selectivity of the single wire predicted by the model. The difference in the integral selectivities does not only arise from the slightly increased averaged Sherwood number, but also from the weighting of the selectivities. This means, that even if the curves for *Sh* in Figure 7.9a were identical for the LES and the laminar case, there would still be a difference in integral N₂O selectivity, as higher N₂O selectivities resulting from higher mass transfer coefficients have a stronger contribution than lower selectivities as a result of lower *Sh*.

7.3.2.5. Transient analysis of surface kinetics

To get an impression on the time scale on which the chemical kinetics take place, the response of the microkinetic model with mass transfer to a perturbation in *Sh* is investigated. To do so, the following procedure is carried out: From the transient data of the single wire LES, the minimum and maximum *Sh* at the front position of the wire are extracted. For the minimum Sherwood number $Sh_{\min} = 0.47$, the kinetics with mass transfer are solved to obtain steady state concentrations near the surface $c_{i,s}^{\min}$ and the surface coverages θ_j^{\min} . Now mass transfer is increased using $Sh_{\max} = 2.93$ and the chemical system is integrated until the new steady state is reached, yielding $c_{s,i}^{\max}$ and surface coverages θ_j^{\max} . For comparison, the micorkinetic model without mass transfer is integrated using the concentrations $c_{s,i}^{\max}$ and starting from θ_j^{\min} as initial conditions. The obtained time evolution of the surface coverages is displayed in Figure 7.10a.

The surface coverages of NH_3 -b, N-a and NO-a are increasing over time, while O is displaced from the surface. In Figure 5.5 it was already demonstrated that the increased mass transfer in the front part of the single wire correlates with increased steady state coverages of N-containing surface species and leading to an increased N_2O selectivity. This is in line with the present results as the new state corresponds to a state of increased mass transfer. According to the profiles, steady state is reached after about 1.5 µs. This time corresponds to the idealized case, where external mass transfer is infinitely fast and is determined by the rates of the elementary reactions only. It is significantly faster than the sampling rate of data in the LES, which is 20 µs. In a real process, however, the gas species near-surface



Figure 7.10.: Time evolution of the surface coverages after a perturbation of the steady state. (a) For the plain kinetic model without mass transfer obtained by the solution of Equation (5.3). (b) For the kinetic model with mass transfer obtained from the solution of Equations (6.15) and (6.16).

concentrations do not adjust instantly, as mass transfer rates are limited. Figure 7.10b shows the time profile of the surface coverages obtained from the kinetic system with mass transfer as previously described. As expected, the steady state surface coverages match those of the system neglecting mass transfer. The time needed to reach steady state increases to about 30 µs, which is slower by a factor of 20. This additional time is attributed to the system adjusting to the new set of surface coverages. On the catalyst surface, the net amount of molecules needs to increase for some species while for other species it needs to decrease in order to reach the new steady state. The site density of the catalyst behaves like a reservoir which needs to be filled or emptied by a certain amount of certain species molecules. The rate of filling and emptying is controlled by the transport rates of gas species from the bulk to the surface of the catalyst and vice versa. It should be noted, that the kinetic model at hand was only validated and parametrized with steady state experimental data [80]. Nevertheless, as surface chemistry is expected to be fast at temperatures typical for industrial ammonia oxidation and the species transport does not depend on details of the kinetic mechanism, the obtained results seem reasonable.

In order to further examine the transient behavior of the kinetic model under mass transfer limitation, the selectivity response to synthetically generated fluctuations in mass transfer are studied. The fluctuations are modeled using sine waves of different frequencies f, ranging from 100 to 5000 Hz, harmonically oscillating between Sh_{min} and Sh_{max} :

$$Sh(t) = \frac{Sh_{\max} + Sh_{\min}}{2} + \frac{Sh_{\max} - Sh_{\min}}{2}\sin(2\pi f t)$$
(7.5)

The resulting response profiles of N₂O selectivity are shown in Figure 7.11a for four different frequencies. The blue dotted line shows the resulting selectivity profile obtained from time integration of Equations (6.15) and (6.16) following the procedure described in section 7.2.2. As a benchmark, the steady state solution at any point in time is plotted in the red curve, reflecting the case of a system with infinite fast chemistry and mass transfer. The integration was carried out for $t = 4T_{per}$, with T_{per} being the periodic time to ensure that, especially at high frequencies, a periodic response is obtained. The plots show the results for the 4th period. For low frequencies of 100 and 500 Hz, mass transfer and surface kinetics are fast enough to follow the fluctuations and the two curves are almost identical. Furthermore, the sinusoidal shape of the input signal in Figure 7.11b is resembled by the selectivity response. This is in line with previous findings, where increased mass transfer intensity caused the



Figure 7.11.: (a) Response of the N₂O selectivity on a harmonically oscillating Sherwood number for different excitation frequencies (dotted blue line). The curves display the data for the fourth period, after a steady oscillating response was obtained. The red line displays the steady state selectivity at every time frame and thus represents the case of an infinite fast surface chemistry and mass transfer. (b) Sinusoidal time evolution of *Sh*.

 N_2O selectivity to rise and vise versa. For 2000 Hz, small deviations with respect to the steady state selectivities can be observed, which become even more pronounced at 5000 Hz. The response is still periodic but not harmonic anymore. Interestingly, the deviations are more pronounced around the selectivity minimum during the second half of the period. As the response time of the system is mainly controlled by the transport of species, for smaller mass transfer coefficients the system needs more time to reach the steady state concentrations and surface coverages.

Due to this increased "inertia" of the system caused by smaller mass transfer coefficients, for higher frequencies the minimum of the N_2O selectivity moves to higher values and later times, leading to a flattening of the curve. These shifts are illustrated in Figure 7.12a. The curve shows the relative deviation of the N_2O selectivity at the minimum from the respective steady state solution as a function of frequency. This deviation increases almost linearly in the range between 1000 and 5000 Hz. Furthermore, the time shift between the minima of the transient and steady state solutions relative to the time of the period (blue diamond markers) is plotted, to illustrate the phase shift of the minimum.

Although these results suggest that at higher frequencies the mass transfer limited kinetics are not able to follow the oscillations in external mass transfer, one has to be aware, that for all exciting frequencies



Figure 7.12.: (a) Relative deviation for the minimum and the phase of the N₂O selectivity obtained from the transient model with respect to the steady state selectivities. (b) Fourier transform of the *Sh* time signal at the front side of the single wire.

the same amplitude in Sh has been used. However, in a real system with turbulent flow, high frequency fluctuations in Sh are caused by smaller sized eddies impinging on the wire surface. Since smaller eddies contain less kinetic energy, their effect on the boundary layer thickness and therefore changes in mass transfer intensity is much weaker compared to larger sized eddies which are correlated to lower frequencies. This is in line with results obtained from the LES. The time evolution of Sh at the front side of the single wire in Figure 7.8a (black curve) reveals that lower frequencies. This becomes even more clear when looking at the Fourier-Transform of the respective Sh time signal shown in Figure 7.12. The spectrum shows a broad range of frequencies for the oscillating Sh with a clear trend of declining amplitude with increasing frequency above about 200 Hz.

7.3.2.6. Summary

Large eddy simulations of an isolated catalyst wire were conducted. The integration of detailed surface kinetics was carried out in a post processing steps. The analysis of the computed velocity field shows that the velocity fluctuations increase when moving upstream away from the catalyst and they are smaller in the shadow of the wire. This lies within the qualitative expectations of a wire in turbulent cross flow. From the frequency power spectrum a smooth transition from lager eddies (low frequencies) to smaller eddies (high frequencies) can be observed, with the turbulent kinetic energy range spanning about 5 orders of magnitude, which indicates a satisfying LES solution.

Strong fluctuations of local Sh with time are observed along the catalyst surface. As indicated by the analysis of the velocity field, these fluctuations in mass transfer are most pronounced at the stagnation point at the front side of the wire and are damped when moving towards the rear side. In line with the degree of mass transfer control analysis in the last chapter, the N₂O selectivity profile qualitatively resembles the profile of Sh, i.e. S_{N_2O} is low when local mass transfer intensity is small and vice versa.

Furthermore, it was found that the species transport to the catalyst surface and the chemical reactions were fast compared to the fluctuations in the flow field, and the chemical system was observed to be in steady state at any time. Thus no special transient effects (such as delaying) regarding the N₂O selectivity were observed. Perturbing the pure mechanistic model with mass transfer using an artificial sinusoidal profile for *Sh*, showed that the response of the chemical kinetics begins trailing the steady state

solution (corresponding to an infinitely fast surface chemistry and mass transfer) at around 2000 Hz. Although the frequencies larger than 2000 Hz can be found in the spectrum of the *Sh* time signal, these frequencies correspond to smaller eddies with kinetic energy too low to significantly perturb the boundary layer around the wire when compared to the larger eddies with lower frequency. Investigating the integral (over time and space) N_2O selectivity, the LES case exhibits only a slight increase (about 0.1% absolute) in selectivity when compared to the respective laminar case.

7.3.3. Multiple wires

In this section the results for the configuration of three rows of parallel catalyst wires are presented. The flow field up- and downstream of the wires is investigated. Then the time-averaged temperature and concentration fields will be compared those obtained from a steady state laminar flow. This is followed by an analysis of how the turbulent flow affects the local mass transfer around the wires and thus the N₂O selectivity. Due to the large amount of data that is created during the LES, the analysis is limited to the central wire of each row. Since for the first and the third row there is no wire in the center of the row, the study is performed at the wire at $y = 12d_w$. Those three wires are labeled "wire 1", "wire 2" and "wire 3", with wire 1 being closest to the inlet (smallest *x*-coordinate). Similar to the single wire case, all data has been collected from a plane at height $z = 20d_w$.

7.3.3.1. Flow regime

As for the case of the single wire, the flow regime for the multi-wire configuration is analyzed at four different positions relative to the catalyst wires. This time the distance is relative to the surface of the central wire in the first row, i.e. wire 1. Figure 7.13 shows the velocity magnitude as a function of time, as well as the RMSE of the velocity magnitude (a) $1d_w$, (b) $2d_w$ and (c) $15d_w$ upstream, as well as $1d_w$ downstream of the wire surface.

Examining the respective profiles, the RMSE decreases when moving along points (c), (b) and (a) towards the front of the first wire, but in contrast to the single wire the RSME is significantly higher inside the gauze at position (d). This increase at position (d) is caused by an increase in flow velocity, due to the channeling effect of the surrounding wires and the confinement and acceleration of the flow. The turbulent vortices are now no longer able to move around the wire. The flow is rather forced through the gaps between the wires. When passing the gap between the wires in the first row, the fluid is directed towards the gaps of the second row. In addition to the confinement, the flow is further accelerated as it heats up when passing the hot wires. This explains the more pronounced amplitudes of the oscillations at position (d), which is located directly in front of the gap in the second row of wires.

To cancel out the acceleration effects due to heating and confinement of the gas, Figure 7.13 also contains the RMSE of the velocity magnitude divided by the average velocity u_m , which is a measure of the turbulence intensity. Here a clear decline of the turbulence intensity can be observed when moving from the free stream towards the gauze. Inside the gauze at point (d), the ratio has dropped to 0.25 compared to 0.72 in the free stream at point (c). This seems reasonable and indicates a laminarization of the flow, as viscous forces become dominant inside the wire configuration, due to the narrow spacing of the wires and the increase in viscosity as a result of higher gas temperatures. Vortices with a size smaller than the wire spacing, which are able to pass through the gap, are mostly dissipated before reaching the slit between the wires in the second row. Due to the back pressure caused by the dense wire configuration, it is furthermore observed, that eddies with a characteristic length larger than the wire distance are stretched in radial direction when moving towards the catalyst. This leads to a flow homogenization and pulsating-like flow throughout a larger part of the catalyst domain.



Figure 7.13.: Velocity magnitude, RSME of the velocity magnitude and RSME of the velocity magnitude divided by the mean velocity u_m at several positions relative to the central wire in the first row. (a) $1d_w$ upstream, (b) $2d_w$ upstream, c) $15d_w$ upstream and d) $1d_w$ downstream of the wire. Note the doubled scale of the y-axis in plot (d) compared to plots (a) – (c). Average inlet velocity is 0.75 m s⁻¹.

The pulsating flow, however, has to be treated with some caution as it may not only be the consequence of local eddies that are stretched orthogonal to the main flow direction. The turbulence generator that is used at the velocity inlet boundary condition may also cause a pulsating flow when generating vortices larger than the size of the whole computational domain. Due to the periodic boundary conditions, the



Figure 7.14.: Power density spectrum recorded at certain distances from the central wire of the first row: (a) one wire diameter upstream, (b) two wire diameters upstream, (c) 15 wire diameter upstream and (d) one wire diameter downstream of the central wire. A sample time of 80 ms and a sampling frequency of 250 kHz was used.

momentum that leaves through one boundary is added to the momentum that enters the domain on the the opposite side, such that the overall momentum inside the domain is conserved. For turbulent structures larger than the size of the domain, this leads to an unrealistic distribution of momentum and artificial pulsations throughout the whole domain. Even vortices that fit into the domain size may cause - to some extent- artificial pulsation inside the gauze, if during the stretching in front of the gauze it hits the boundaries of the domain, i.e some radial momentum of the vortex goes through the boundary. In such a case, the domain would be to small to reproduce a realistic distribution of momentum throughout the gauze. To check, whether the size of the domain chosen in this study is too small, the results need to be compared to simulations with a larger computational domain. This, however, requires an even higher numerical effort than for the present study and was not carried out in this work. One way to reduce the computational costs and allow efficient scaling of the domain would be to represent the catalyst as a homogeneous porous medium. Unfortunately, the transition of turbulent to laminar flow when entering a porous medium is only barely covered in the literature. For monolith converters used in exhaust gas after treatment this effect has been studied in [156] [157].

The PSD at the 4 different positions are plotted in Figure 7.14. The energy content in the spectrum spans several orders of magnitude, indicating that the LES resolves a sufficiently large fraction of turbulent kinetic energy. The energy containing range (low frequencies) at position (d) is shifted to

higher energies by about one order of magnitude, as due to the acceleration of the fluid inside the catalyst its kinetic energy is increases. Furthermore, a fast decay in the energy content occurs at a frequency of about 300 Hz, indicating a missing energy cascade over a series of vortices of many different sizes, which is typical for an unsteady laminar flow regime, thus confirming the conclusion of flow laminarization within the wire configuration. Since this laminarizing effect is not present for the single wire, the respective frequency spectrum in Figure 7.5d exhibits a different shape, more characteristic for turbulent flow. In total, almost all of the total kinetic energy is resolved and only a small part is modeled within the subgrid-scale model.

7.3.3.2. Temperature and concentration field

Figure 7.15 shows the temperature and NH₃ mole fraction fields along a plane at $z = 10d_w$. For the LES an instantaneous time frame at t = 30 ms, as well as a time average over 100 ms is shown. The figure also contains the respective fields obtained for a steady state laminar flow.



Figure 7.15.: Temperature (top row) and NH₃ mole fraction (bottom row) obtained from (a) a laminar steady state simulation, (b) the time-averaged LES and (c) an instantaneous frame of the LES.

As expected, for laminar and turbulent flow, mass and heat transfer limitations are observed, with strong gradients especially pronounced around the wires in the first row. In line with the results of the two-dimensional 10 wire model, most of the ammonia is consumed already after the third wire. Hardly any difference is noticed, when comparing the temperature and mole fraction profiles obtained from

the LES at an instantaneous time frame with those from the laminar flow and the time-averaged LES solution. This is an interesting result, as for the single wire case, non-symmetric and chaotic profiles were observed for the instantaneous LES frame. The almost symmetric distribution is a consequence of the flow homogenization due to the close wire spacing, as discussed in the previous section.

7.3.3.3. Mass transfer

In order to quantify the effect of the turbulent flow on the local mass transfer rate of ammonia to the catalyst surface, the local Sherwood number is plotted along the perimeter of the three wires for different time frames in Figure 7.16.



Figure 7.16.: Sherwood number along the perimeter of the wires for different points in time.

Each wire is part of a different row, i.e. wire 1 is located in the first row, wire 2 in the second etc.. Unlike profiles obtained for the single wire shown in Figure 7.9, for all three wires, the shape of the curves for Sh at different time points look quite similar, being shifted along the y-axis. The shift and the similarity of the curves is a result of the homogenization and the pulsating nature of the flow throughout the catalyst. In all time frames the maximum in mass transfer is located at the front of the wire while the lowest Sh is observed at the rear side, resembling the laminar case. The only exception is the curve along wire 1 at 12 ms, where the maximum is shifted further to the back of the wire. In this case, the flow attacks the wire at a slightly skewed angle. The shape of the respective curve at 12 ms around wire 2 indicates, that the flow is homogenized, already before passing through the second row of wires.

The local Sherwood number as a function time at three different locations on the catalyst wires is plotted in Figure 7.17a. Due to the time-resolved fluctuations of the flow field, local Sh around the different wires also shows large variations. Although these variations are very pronounced at all three positions and on all wires, there are some trends to be noticed: Maximum mass transfer intensities are observed in front of the second wire, which is in line with the laminar results and explained by the channeling of the flow when passing the gap of the first wire row and being accelerated towards the stagnation point of the wires in the second row. For all wires, on average, highest Sherwood numbers are observed at the front, then declining towards the rear, which is an expected result for a laminarized flow. Over the full sampling time, there are only a few exceptions, exclusively on the first wire, where Sh at the "Top" position is almost equal to, or even slightly exceeds the value observed at the "Front" position. This occurs only if the direction of the local flow field around the first wire deviates from the direction of the main flow (x-direction). Due to the laminarization effect of the wire configuration, this seems to be the case only occasionally and is not observed for the wires in the second and third row. The effect of the laminarized flow can also be observed when comparing Sh of the multi-wire case with those of the single wire in Figure 7.8a. Between profiles at the different sample positions "Front", "Top"



Figure 7.17.: (a) Sherwood number extracted from the LES and (b) N₂O selectivity calculated with the 0dimensional model as a function of time at three different positions along the wire surface: front side (red), on top of the wire (red) and at the rear side (blue). The results are shown for all three wires.

and "After" there is less statistical correlation in case of the isolated wire, especially when compared to the profiles at wire 2 and wire 3 in Figure 7.17a.

Although the maximum Sherwood numbers at the front side are predicted to be higher on the second wire when compared to the first wire, this does not hold true if the respective Sh gets small. At the front side lower values for Sh are found at the second wire when compared to the first wire, which at first glance seems to be contradictory. And in fact this is a result of the way, the mass transfer coefficients are defined. The ammonia concentration at the inlet of the domain is used as bulk concentration for the calculation of β in Equation (6.46). Small Sh are caused by very small flow velocities leading to higher residence times so that more ammonia is consumed at the first wire. This reduces the flux of ammonia towards the second wire R_i while $(c_{b,i} - c_{s,i})$ stays almost constant. Since this effect only occurs at low Sh the impact on the integral N₂O selectivity however is small.

The respective N_2O selectivity calculated with the 0-dimensional model is plotted in Figure 7.17b. For all wires, at all three positions, the curves of the selectivity qualitatively matches those of the respective
Sh in Figure 7.17a. This is a first indication that also in the case of multiple layers of parallel wires the surface chemistry under mass transfer limitation is fast enough to follow the fluctuations in Sh caused by the turbulent flow field. Thus, the system is in quasi-steady at all time frames. This assumption is confirmed when comparing the selectivities in Figure 7.17b with the ones obtained by the respective steady state solution of Equations (6.15) and (6.16). Again the RMSE of the N₂O selectivity is weighted with the local rate of ammonia consumption and averaged over all locations and time frames. The resulting error of 0.00078% indicates negligible deviations from the steady state solution and thus a fast chemistry following the fluctuations in Sh.

7.3.3.4. Influence on N₂O selectivity

In order to investigate the results on an integral scale, time- and spatial-averaged quantities from the LES need to be considered. The (arithmetic) time average of the Sherwood numbers along the perimeter of the three different wires are plotted in the top row of Figure 7.18. The plots also contain *Sh* predicted by the simulation of laminar flow.

For all three wires the two flow models predict very similar Sh along the wire perimeter. The maxima in mass transfer intensity are observed at the front and minima at the rear of the wire. In contrast to the single wire case, here the deviations between the model predictions are less pronounced. Again this can be attributed to the flow being laminarized when entering the wire configuration. While for the first wire the LES and the laminar simulation predict almost equal Sh in the frontal area of the wire, around the second wire Sh is higher in case of laminar flow. The slightly lower Sherwood numbers obtained in case of the LES are due to time frames with lower flow velocities and high residence times, where most of the ammonia is converted at the first wire. As the mass transfer coefficient was defined using the NH₃ concentration at the inlet, small Sh are predicted slightly too low. The previous results indicating that the flow is of laminar character inside the wire configuration are consolidated by the similarity of the Shcurves from the laminar and the LES case. The congruent profiles around wire 3 confirm this statement.

The corresponding curves for N_2O selectivities are shown in the bottom row of Figure 7.18. For the LES average, the selectivities are weighted with the respective rate of ammonia consumption according to Equation (7.4). Around the first wire, similar selectivities are obtained for both models. For the second wire more N_2O is produced in case of the LES when compared to the laminar case. This seems to contradict the respective profiles of *Sh*. As the N_2O selectivity exhibits a positive degree of mass transfer control, for higher *Sh*, increased selectivities are expected. However, one has to keep in mind, that the selectivities in case of the LES are a time average that has been weighted with the rate of NH_3 consumption. Thus selectivities occurring at higher *Sh* need to be weighted stronger than those at lower *Sh*, leading to a slightly increased selectivity in case of the LES. This effect also explains the selectivity ranking observed around the third wire.

The integral results over the all wires can be obtained by averaging the selectivities over all wire positions on all wires, again weighted with the respective rate of ammonia consumption. In case of the LES, the index i in Equation (7.4) now runs over all time time frames and all surface elements of all three wires. The results are summarized in Table 7.3.

Table 7.3.: Integral selectivities over the three wires of the multi-wire configuration obtained for the laminar simulation and the LES.

Flow model	$S_{ m N_2O}^{ m I}$ / %
Laminar	1.70
LES average	1.78



Figure 7.18.: Comparison of laminar flow and time-averaged LES. Top row: Sherwood number along the wire perimeter of the central wires in the first, second and third row. Bottom row: N₂O selectivity along the perimeter of the wires.

As already indicated by the selectivity profiles in Figure 7.18, there is not much difference in the integral selectivities predicted by the LES compared to the laminar flow. Similar to the single wire case, the difference in selectivity is less than 0.1% absolute between the LES and the laminar flow. The deviations are mostly caused by the differences around the second wire and the effect of weighting the selectivities. With the fast chemistry following the turbulence-induced fluctuations and the average mass transfer intensity being almost equal to the laminar case, the models predict the influence of the turbulent flow field on the product selectivity more or less to be averaging out. The necessary weighting of the selectivities is the only effect that remains, although being not very pronounced.

In the case of both, laminar as well as turbulent flow, the N_2O selectivity is higher for the multi-wire case compared to the single wire (compare to Table 7.2). Due to the laminarizing effect of the multi-wire configuration one would expect a slightly higher mass transfer intensity and thus N_2O selectivity for the single wire case. This effect however is surpassed by the confinement of the fluid and the resulting increased mass transfer rates inside the multi-wire configuration. Comparing the Sherwood numbers in Figure 7.9 and 7.18 it is observed that due to the fluid acceleration already at the front and middle part of the first wire, *Sh* is higher compared to the single wire. Compared with the second wire the difference becomes even more pronounced, especially at the stagnation points of the wire.

7.3.3.5. Influence of larger sized eddies

This work was focused on the investigation and discussion of coherent structures that are about or less the size of the domain (which is a few millimeters) and their effect on the mass transfer limited ammonia oxidation reaction. In a real reactor with several meters in diameter, larger eddies are expected to occur in the flow upstream of the catalyst. These larger sized vortices may also influence the performance of the first catalyst layers. Since they are of larger size, the respective fluctuations in the velocity field are shifted to lower frequencies compared to the smaller sized eddies studied in this chapter. Thus, for those larger scale structures the surface chemistry will definitely be able to follow the *Sh* fluctuations. On the scale of the catalyst wires, these eddies will result in a pulsating flow throughout the domain, which is statistically oscillating around the mean flow velocity. If sampled long enough, this will lead to an average *Sh* equal to that produced by laminar flow with the same average flow velocity. Compared to the laminar case, the only effect on the N₂O selectivity that does not completely average out is again the fact, that the selectivities observed at higher mass transfer rates need to be weighted stronger. As it was demonstrated at the smaller scale, this effect is not very pronounced. If one has information on the turbulent velocity field at the larger scale, this phenomenon can very easily be quantified using unsteady laminar gauze scale simulations. One can also estimate this effect by applying a periodically oscillating inlet velocity of different amplitudes and frequencies. Due to the arguments outlined above, only a minor difference to the steady state laminar case are expected.

7.3.3.6. Effect on catalyst temperature

The influence of turbulent flow on the temperature of the wires was not investigated in this work but can be discussed qualitatively. It was already shown in section 5.4.2 that the temperature of the first wires is controlled by the Lewis number of the reactive flow. As the Lewis number only depends on physical properties of the fluid itself, it should not be affected by the turbulent fluctuations of the flow field. It does only change slightly as the composition of the fluid changes due to chemical reactions. Furthermore the ratio of Sherwood and Nusselt number only varies slightly over time, indicating that mass and heat transfer are equally fluctuating with the turbulent flow field. Therefore, there should be no temperature variation in the catalyst temperature due to a change in Lewis number. In section 5.4.1 it was demonstrated that the temperature of the wire is not only dictated by the Lewis number of the fluid but also by the conversion per wire. For a Lewis number below unity, the temperature of the first wire increases if the conversion around the wire decreases. The maximum wire temperature is reached in case of infinitesimal small conversion and is given by Equation (5.17). For low Sh the residence time of the gas in the catalyst increases. Thus the conversion per wire increases and the wire temperature drops. If the fluid velocity around the wire increases, the conversion per wire declines and the temperature moves towards the maximum temperature. In the models used in this work, these temperature fluctuations are in the range of about 30 K, confined by the adiabatic temperature (low local velocity, high residence times, full conversion after the first wire) and the maximum temperature given by Equation (5.17) (high velocities, short residence times, almost no conversion). It is important to notice that this temperature range depends on the chosen data for species diffusion coefficients and thermal conductivity as discussed previously in section section 5.4.1. How strong the variation of the wire temperature in between the discussed limits will be, mainly depends on the heat capacity of the platinum wires. If c_p is large compared to the heat transfer rates, the temperature will not change significantly over time. The fact that the selectivity distribution is a function of mass transfer intensity may also impact the wire temperature as the reactions towards the different products exhibit different enthalpies of reaction (for instance the reaction towards N₂O is more exothermic than the reaction to NO by about 142 kJ per mole of consumed NH_3). Due to the generally small changes in selectivity, however, this effect should not be dominant.

To asses the variations in wire temperature with reasonable numerical effort, one could perform unsteady laminar simulations using the geometry of Figure 5.7. Since the highest amplitudes in the oscillating Sh profile in Figure 7.17 are associated with the low frequency parts of the turbulent flow field, in these simulations the inlet velocity could be varied in such a way that the low frequency oscillations in Sh are reproduced. Furthermore it would not be necessary to incorporate the full kinetic model into

the flow simulation, a first order reaction approach, as used in the LES in this work, would be sufficient.

An exact spacial and transient temperature profile, however, can only be obtained from a simulation in which one solves for the temperature of the wires and incorporates the full kinetic model into the LES, which is out of the scope of this work.

7.3.3.7. Summary

The study on the effect of upstream turbulence on the catalytic performance of an isolated Pt-cylinder, presented in section 7.3.2, has been extended to a configuration of 3 parallel and staggered rows of catalytic wires. Due to an increase in fluid temperature as well as the confinement due to the configuration of the catalyst wires, a mostly laminarized, but still unsteady, flow was observed already at the second row of wires. The back pressure created by the densely packed wire configuration caused larger scale eddies to stretch out in the direction perpendicular to the main flow, resulting in a homogenized and pulsating-like flow throughout the catalyst. It was found, that almost all of the ammonia is consumed after the third wire.

Fluctuations of Sh with time are observed along the surface of all catalyst wires. These fluctuations in mass transfer intensity are most pronounced at the stagnation point at the front side of the wires and are damped when moving towards the rear side. Similar to the case of laminar flow, the channeling effect of the first wire row accelerates the fluid towards the stagnation point of the second wire, this time, superimposed with the temporal fluctuations of the velocity field due to upstream turbulence. Thus the highest values for Sh are observed at the front side of the second wire. Again, due to a positive degree of mass transfer control for S_{N_2O} , the N₂O selectivity profile qualitatively follows the profile in mass transfer intensity.

The simulations showed the chemical reactions on the surface to be in quasi-steady state at all times, thus no transient delaying effects regarding the N_2O selectivity could be observed for the multiwire configuration. Also the integral selectivity is found to only slightly increase by about 0.08% when compared to the laminar case. Furthermore, it was reasoned that turbulent structures, with a size exceeding the scales of the studied domain and thus not being accounted for in the current investigations, would appear as pulsating velocity field inside that very domain. Since this pulsating field would statistically fluctuate around that of the respective laminar case, on average, the same mass transfer intensities would be observed. The weighting of the selectivity with the instantaneous mass transfer rate would be the only effect that would not average out. Since this effect is found to be small in the current simulations, it is estimated to do so in case of larger eddies as well.

Finally, it was reasoned that a fluctuating velocity field would affect the catalyst temperature mostly due to the resulting changes in the conversion per wire. The maximum temperature fluctuations possible are given by the Lewis number of the fluid and with the model used in this work, these fluctuations were estimated not to exceed 30 K.

7.4. Conclusion

Industrial ammonia oxidation is carried out in large reaction vessels with diameters spanning up to several meters. Due to the size of the reactor, the Reynolds number of the flow upstream of the gauze catalysts is estimated to be in the order of 10^5 , thus the flow is assumed to be highly turbulent. In this chapter, large eddy simulations of turbulent flow around Pt wires, coupled with a microkinetic model describing the chemistry on the wire surface, have been used to investigate the influence of upstream turbulent flow on the performance of Pt catalyst wires, a topic that has not been investigated in great detail so far. Cornejo [158] investigated the interaction of upstream turbulent flow on monolith catalyst

structures for automotive applications, but did not focus on the interaction between flow and surface chemistry. In general, there seems to be only little work on this topic, and along with the study of Fadic [125] this is the only work combining the solution of detailed surface kinetic models with the computation of temporal resolved turbulent flow around structured catalysts.

It was shown that the turbulent structures have decayed to a great extent already after the first row of wires, resulting in an unsteady laminar and pulsating-like flow throughout the catalyst gauze. The fluctuations in the velocity field caused time-dependent variations of mass transfer intensity along the catalyst surface. The profile in N₂O selectivity resulting from these fluctuations can again be explained with the degree of mass transfer control: Due to a positive X_{SC,β,N_2O}^m , local and temporal perturbations of the velocity field that lead to an increase in mass transfer intensity cause an increase in S_{N_2O} . The fluctuations in N₂O selectivity caused by the turbulent nature of the flow were superimposed with the local variations observed in the case of laminar flow. As a result, the trends for the distribution of relative N₂O production rates derived from the time-averaged turbulent simulation remain the same when compared to the case of laminar flow, which were discussed in chapter 5: Along the wire surface, on average the model predicts the highest S_{N_2O} at the tip of the wire, decreasing towards the back-end. Throughout the catalyst, (on average) the highest mass transfer rates and thus the maximum in N₂O selectivity are located at the tip of the wire in the second row. From simulations of an isolated single wire it was found, that the relaxation of the network of chemical reactions and near-surface concentrations was fast compared to the time scale of the fluctuations in external mass transfer intensity. Therefore the chemical system was found in quasi-steady state at any time and no delay in N₂O selectivity response with respect to fluctuations in Sh was observed. Compared to the results obtained with laminar flow, only minor differences in the overall integral selectivity of N2O formation have been predicted by the LES for the single wire, as well as for the configuration of multiple wires. The minor increase in selectivity is the result of both a slightly higher average Sh and the weighting of the local selectivities with the respective NH₃ consumption rate.

The simulation results presented in this chapter are a first indication, that the presence of turbulent flow inside the industrial reactor lead only to a minor increase in N₂O compared to the case of laminar flow. However, it needs to be emphasized that the study presented in this work is the first of its kind and still leaves several open questions. First of all, further work is needed to clarify, if the pulsating flow throughout the catalyst is root of an unrealistic momentum distribution in the domain, which is artificially caused by choice of a too small domain size. This artificial pulsation would lead to an overestimation of local mass transfer intensities and its influence on the chemical behavior of the system requires further investigations. This also accounts for the influence of turbulent flow on the catalyst temperature. This effect has only been discussed qualitatively, giving an estimation on maximum temperature fluctuations possible. But again, without further calculations, no robust statements about consequences for the N_2O selectivity can be given. In this work, cases with idealized catalyst geometries have been examined. The behavior of the catalytic system under observation is controlled by the complex interaction of a variety of physical and chemical phenomena. Taking into account the chaotic nature of turbulent flow, the use of more complex catalyst shapes may lead to some unexpected effects with an influence on product selectivity, exceeding that reported in this work. In addition, putting more experimental effort in the accurate determination of $n_{S_{N_2O},c_{NH_2}}$, i.e. the sensitivity of N₂O selectivity with respect to the NH₃ near-surface concentration, would make models more robust towards the prediction of absolute selectivities and thus allow to quantify the response of the chemical system towards reactor-scale turbulent effects with higher accuracy.

If further studies confirm the results of this work, future simulation work and investigations dedicated to investigate ammonia oxidation catalysts under industrial conditions may neglect turbulence effects

thus leaving laminar flow to be a valid assumption. This of course would greatly reduce the numerical effort of simulation studies to come. On the other hand, such findings might deprive plant operators of the opportunity to actively control the process selectivity by upgrading ammonia burners with respective installations, that dampen or increase turbulent intensity of the flow upstream of the catalyst gauzes to their advantage.

8. Summary and concluding remarks

Together with the Haber-Bosch process the Ostwald process forms the chemical backbone to cover the high demand of fertilizers of a still growing world population. Due to the large scale of the process, small improvements in NO selectivity during industrial ammonia oxidation can lead to significant savings in energy consumption and emission of greenhouse gases, such as CO_2 and N_2O . Optimizing the efficiency of such a large scale process can make a large contribution to the reduction of greenhouse gas emissions. Investigations on Pt-based NH₃ oxidation catalysts have been conducted by the means of numerical models with the aim to generate a more detailed understanding of the influence of certain process parameters on the selectivity of the catalyst. Special focus was set on the interplay between fluid flow, catalyst geometry, external mass transfer and surface chemistry. To describe the chemical reactions for ammonia oxidation on the surface of the Pt catalyst, published microkinetic models have been used. The respective chemical rate equations have been solved together with balance equations for mass, momentum, energy and species, yielding the velocity-, concentration- and temperature field throughout the catalyst domain.

With two-dimensional simulations of catalytic wires it was shown that the local N₂O selectivity is varying along the perimeter of the Pt wires, exhibiting a maximum at the front side and decreasing towards the rear. Furthermore, N₂O selectivity was observed to increase with a shrinking wire diameter, a decreasing wire-to-wire distance and when positioning the wires in the second row behind the opening cross sections of the first wire row. All these effects are controlled by $n_{S_{N_2O},c_{NH_3}}$, i.e. the sensitivity of N₂O selectivity with respect to near-surface ammonia concentration, together with the distribution of c_{NH_3} along the catalyst surface. The latter is governed by the local mass transfer intensity, while the concentration distribution of the remaining reactants O₂ and NO remains unaffected. Although a positive $n_{S_{N_2O},c_{NH_3}}$ seems reasonable, it still depends on the details of the mechanistic model being used, and other models may predict a negative value. Therefore, future experimental and mechanistic work should focus on a more precise determination of this sensitivity coefficient. This is a good example, how the utilization of reactor modeling with detailed chemistry can assist and guide future experimental work.

Independent from the mechanistic model used, it was demonstrated that the temperature of the first wires in the gauze is a function of the Lewis number of the gas. A gas with a Lewis number below unity will cause the temperature of the front wires to exceed the adiabatic temperature. This effect is more pronounced, the smaller the ammonia conversion per wire, as it is the case at higher operating pressure. The upper limit for the temperature of the first wire is given by the Lewis number. Due to uncertainties in the physical properties (thermal conductivity and diffusion coefficients) used in this model, a more precise determination of the fluids' Lewis number would help to better quantify the temperature increase of the first wires. Based on the results generated in this work, it can be suggested to also put effort in determining the temperature distribution throughout the gauze. If the first gauzes are indeed found to be at a higher temperature, as indicated by the model, then this effect might be an explanation for the increased precious metal losses that is observed especially when the process is carried out at elevated pressures.

In order to perform a correct and quantitative degree of rate control analysis for a heterogeneously catalyzed system that is in the mass transfer limited regime, it has been demonstrated, that the set of equations describing the chemical network needs to be extended by additional equations accounting for mass transfer. Using the case of industrial ammonia oxidation as an example, the degree of rate control analysis of the kinetics including external mass transfer $X_{\rm RC}^m$ has predicted the sensitivities with almost the same accuracy as one would obtain them from a full CFD reactor model, but only at a fraction of the numerical effort. Furthermore, a calculation technique for $X_{\rm RC}^m$ has been presented utilizing the Jacobians of the chemical rates, resulting in speed up factors of about 20 compared to the numerical integration of the system of differential equations. The concept of degree of mass transfer control $(X_{SC,\beta}^m)$, i.e. the sensitivity of product selectivity with respect to mass transfer intensity, manifests a more direct link between changes in species mass transfer and product selectivity distribution. Both N₂O and N₂ have been found to have a positive $X_{SC,\beta}^m$ for the investigated reaction kinetic models. Together with CFD simulations of resolved catalyst geometries, the degree of mass transfer control states a novel and unique tool for the investigation and rational design of structured catalysts. This type of investigation is not limited to industrial ammonia oxidation but can in principle find utilization in any high temperature process where selectivity is a function of local mass transfer.

The rationale behind this tool is that the CFD simulations predict the distribution of mass transfer intensities along the catalyst surface, while the $X_{SC,\beta}^m$ quantify how the changes in local mass transfer effect the distribution of product selectivity. The CFD model does not need to contain any details about the surface chemistry, which makes it much more efficient to solve. Besides the numerical advantage, it allows to quickly investigate different sets of kinetic parameters or even different mechanistic models for the same catalyst geometry, as this only affects the $X_{SC,\beta}^m$ analysis.

The usefulness of this novel concept was shown applying it to three-dimensional models of a woven gauze as well as a restructured Pt wire derived from μ -CT images. In both applications the predictions of the novel approach regarding the distribution of product selectivity as a function of mass transfer intensity have qualitatively matched those obtained from full CFD calculations including all chemical details. The combined analysis supported the findings of the two-dimensional simulations, i.e. that increasing mass transfer leads to higher N₂O and N₂ selectivities. Analyzing each individual layer of a package of woven gauzes revealed that those layers showed an improved performance (i.e. lower N₂O selectivity) on which areas with lower mass transfer coefficients exhibited a higher contribution to the overall conversion. Based on these results, catalyst design for industrial ammonia oxidation should focus on minimizing mass transfer intensities around the catalyst wires. In addition, this analysis presents a mechanistic explanation, why the nowadays widely spread knitted gauzes outperform catalyst gauzes of woven form. This was previously only based on a heuristic reasoning.

Large eddy simulations of reactive flow around a single catalytic wire, as well as a staggered configuration of multiple wires have been conducted in order to access the influence of upstream turbulence on the performance of the catalytic process. In order to minimize the computational effort, the integration of the surface chemistry has been decoupled from the solution of the Navier-Stokes equations and was performed in two subsequent steps. To the authors knowledge, besides the study of Fadic [125], this was so far the only work that combines mechanistic surface kinetics with the simulation of timeresolved turbulent flow. Furthermore, it presents a novel approach to efficiently include detailed surface chemistry into simulations of turbulent flow around catalyst in mass transfer controlled processes. The investigations of the catalytic single wire revealed that, with the microkinetic model used in this work, the transport of species to the catalyst surface and the chemical reactions on the surface occur on a shorter time scale, than the fluctuations of the flow field. As a consequence, the chemical system was found to be in quasi-steady state at any time, thus no special transient effects with regards to the N₂O selectivity are observed.

For both simplified catalyst configurations, the models predicted only a minor increase in N_2O selectivity in the presence of turbulent flow compared to laminar flow. This result, however, should rather be considered as a first indication than a final conclusion for several reasons:

- 1. For a more robust quantification of the influence of external mass transfer intensity and thus turbulent flow on the N₂O selectivity, a more precise determination of $n_{S_{N_2O},c_{NH_2}}$ would be required.
- 2. In case of the multi-wire configuration further work should be dedicated towards clarifying the influence of the size of the computational domain. It needs to be accessed if the choice of a too small domain size leads to an unrealistic momentum distribution and artificial pulsation of the flow throughout the domain investigated and if this has a significant impact on the overall results. If this should be the case, a larger, more characteristic section of the catalyst gauze needs to be considered, involving higher computational effort.
- 3. The effect of a fluctuating flow field on the temperature of the catalyst wires has only been discussed qualitatively in this study. The maximum temperature fluctuation of the wires is determined by the Lewis number of the fluid and was estimated not to exceed 30 K in this work. Other models may predict a different temperature window, as *Le* depends on the chosen model and data for the physical properties of the fluid (in this case diffusion coefficients and thermal conductivity). Assuming an uncertainty of 10% for the literature species transport data, fluctuations of more than 60 K are also possible. As the catalyst temperature is known to have a strong influence on the selectivity of the process, more detailed investigations are required.
- 4. Due to the complexity of the overall system and non-linearity of the underlying chemical and physical processes, for more complex gauze geometries unexpected phenomena, exceeding those found and discussed in this work might be observed.

Despite leaving several open questions and not providing the definite answer to the question whether upstream turbulence has an impact on the selectivity of industrial ammonia oxidation, the work presented already gives important insights and qualitative results. In addition, it presents an efficient numerical framework for further investigations dedicated towards answering this questions.

A. Polynomial coefficients for transport properties

A.1. Heat capacity

The specific heat capacity at constant pressure of species i as a function of temperature is given by the following polynomial:

$$c_{p,i} = a_i + b_i T + c_i T^2 + d_i T^3 + e_i T^4$$
(A.1)

The respective polynomial coefficients are summarized in Table A.1.

Table A.1.: Polynomial coefficients for the temperature-dependent specific heat capacity at constant pressure taken from [43].

Species	a / J kg ⁻¹ K ⁻¹	b / J kg $^{-1}$ K $^{-2}$	c / J $\rm kg^{-1}~\rm K^{-3}$	d / J kg $^{-1}$ K $^{-4}$	e / J $\rm kg^{-1}~K^{-5}$
NH ₃	1974.9	$-7.4006 \cdot 10^{-1}$	$5.2298 \cdot 10^{-3}$	$-4.2225 \cdot 10^{-6}$	$1.0923 \cdot 10^{-9}$
O_2	922.9	$-2.7812 \cdot 10^{-1}$	$1.1901 \cdot 10^{-3}$	$-1.0196 \cdot 10^{-6}$	$2.7690 \cdot 10^{-10}$
H_2O	1885.1	$-4.6770 \cdot 10^{-1}$	$1.6614 \cdot 10^{-3}$	$-9.9028 \cdot 10^{-7}$	$2.0519 \cdot 10^{-10}$
NO	1107.6	$-7.8753 \cdot 10^{-1}$	$1.7719 \cdot 10^{-3}$	$-1.2619 \cdot 10^{-6}$	$3.0399 \cdot 10^{-10}$
N_2O	527.7	1.4087	$-8.6339 \cdot 10^{-4}$	$1.5834 \cdot 10^{-7}$	$1.8505 \cdot 10^{-11}$
N_2	1047.9	$-1.2641 \cdot 10^{-1}$	$3.5986 \cdot 10^{-4}$	$-1.5399 \cdot 10^{-7}$	$9.2625 \cdot 10^{-12}$
H_2	11759.0	9.3417	$-1.7847 \cdot 10^{-2}$	$1.4759 \cdot 10^{-5}$	$-4.0549 \cdot 10^{-19}$

A.2. Viscosity

The dynamic viscosity of species i as a function of temperature is given by the following polynomial:

$$\mu_i = a_i + b_i T + c_i T^2 + d_i T^3 \tag{A.2}$$

The respective polynomial coefficients are summarized in Table A.2.

Species	a / Pa s	b / Pa s K $^{-1}$	c / Pa s K $^{-2}$	d / Pa s K $^{-3}$
NH ₃	$-7.6819 \cdot 10^{-7}$	$3.6699 \cdot 10^{-8}$	$-4.7132 \cdot 10^{-13}$	$4.8010 \cdot 10^{-17}$
O_2	$-4.9433 \cdot 10^{-7}$	$8.0673 \cdot 10^{-8}$	$-4.0416 \cdot 10^{-11}$	$1.0112 \cdot 10^{-14}$
H_2O	$2.2821 \cdot 10^{-6}$	$1.7387 \cdot 10^{-8}$	$3.2465 \cdot 10^{-11}$ ·	$-1.4334 \cdot 10^{-14}$
NO	$-6.2427 \cdot 10^{-8}$	$7.3843 \cdot 10^{-8}$	$-3.7605 \cdot 10^{-11}$	$9.2672 \cdot 10^{-15}$
N_2O	$-1.5241 \cdot 10^{-6}$	$6.1281 \cdot 10^{-8}$	$-2.4874 \cdot 10^{-11}$	$5.3160 \cdot 10^{-15}$
N_2	$4.4656 \cdot 10^{-7}$	$6.3814 \cdot 10^{-8}$	$-2.6596 \cdot 10^{-11}$	$5.4113 \cdot 10^{-15}$
H_2	$1.7611 \cdot 10^{-7}$	$3.4165 \cdot 10^{-8}$	$1.8368 \cdot 10^{-11}$	$5.1147 \cdot 10^{-15}$

Table A.2.: Polynomial coefficients for the temperature-dependent dynamic viscosity taken from [159].

A.3. Thermal conductivity

The thermal conductivity of species i as a function of temperature is given by the following polynomial:

$$\lambda_i = a_i + b_i T + c_i T^2 + d_i T^3 + e_i T^4 + f_i T^5$$
(A.3)

The respective polynomial coefficients are summarized in Table A.3. The coefficients were obtained by fitting the viscosity calculated from kinetic theory as described in section 3.3.4. The coefficients were obtained by fitting the viscosity calculated from kinetic theory as described in section 3.3.4. The coefficients for H_2 are taken directly from [159].

Table A.3.: Polynomial coefficients for the temperature-dependent species thermal conductivity.

Species	a / W m ⁻¹ K ⁻¹	b / W m ⁻¹ K ⁻²	c / W $\rm m^{-1}~K^{-3}$	d / W m ⁻¹ K ⁻⁴
NH ₃	$-2.1106 \cdot 10^{-2}$	$1.9898 \cdot 10^{-4}$	$-2.0728 \cdot 10^{-7}$	$3.3880 \cdot 10^{-10}$
O_2	$8.8090 \cdot 10^{-3}$	$5.2622 \cdot 10^{-5}$	$4.7915 \cdot 10^{-8}$	$-6.1115 \cdot 10^{-11}$
H_2O	$1.1468 \cdot 10^{-2}$	$-2.6617 \cdot 10^{-4}$	$2.0713 \cdot 10^{-7}$	$-1.4016 \cdot 10^{-10}$
NO	$5.7448 \cdot 10^{-3}$	$8.0917 \cdot 10^{-5}$	$-3.6305 \cdot 10^{-8}$	$5.5877 \cdot 10^{-11}$
N_2O	$-5.6534 \cdot 10^{-3}$	$7.9628 \cdot 10^{-5}$	$7.0979 \cdot 10^{-9}$	$-9.0100\cdot 10^{-12}$
N_2	$-3.7199 \cdot 10^{-3}$	$1.4442 \cdot 10^{-4}$	$-2.2182 \cdot 10^{-7}$	$2.7254 \cdot 10^{-10}$
H_2	$1.0979 \cdot 10^{-2}$	$6.6411 \cdot 10^{-4}$	$-3.4378 \cdot 10^{-7}$	$9.7283 \cdot 10^{-11}$
		1 1	1 0	

Species	e / W m ⁻¹ K ⁻⁵	f / W m ⁻¹ K ⁻⁶
NH ₃	$-2.2265 \cdot 10^{-13}$	$5.1929 \cdot 10^{-17}$
O_2	$2.8163 \cdot 10^{-14}$	$-4.4852 \cdot 10^{-18}$
H_2O	$5.2904 \cdot 10^{-14}$	$-6.6502 \cdot 10^{-18}$
NO	$-4.4702 \cdot 10^{-14}$	$1.2339 \cdot 10^{-17}$
N_2O	$-5.5072 \cdot 10^{-15}$	$3.6755 \cdot 10^{-18}$
N_2	$-1.6241 \cdot 10^{-13}$	$3.6779 \cdot 10^{-17}$
H ₂	0.0000	0.0000

A.4. Binary diffusion coefficients

The binary diffusion coefficient of species i and j as a function of temperature is given by the following polynomial:

$$D_{ij} = a_{ij} + b_{ij}T + c_{ij}T^2 + d_{ij}T^3 + e_{ij}T^4 + f_{ij}T^5$$
(A.4)

The respective polynomial coefficients for all pairs of species are summarized in Table A.4. The polynomial coefficients were obtained by fitting the binary diffusion coefficients calculated from kinetic theory as described in section 3.3.4. All coefficients involving H_2 were fitted to Equation (3.24) with Lennard-Jones parameter taken from [160].

		•	
Species	$a \neq \mathrm{m}^2 \mathrm{~s}^{-1}$	$b \neq m^2 s^{-1} K^{-1}$	$c \neq m^2 s^{-1} K^{-2} = d \neq m^2 s^{-1} K^{-3}$
NH ₃ - O ₂	$-6.7332 \cdot 10^{-7}$	$6.7594 \cdot 10^{-9}$	$4.3538 \cdot 10^{-11} \ -1.6785 \cdot 10^{-14}$
NH ₃ - H ₂ O	$4.6301 \cdot 10^{-6}$	$-3.9935 \cdot 10^{-8}$	$1.4333 \cdot 10^{-10} \ -1.7657 \cdot 10^{-13}$
NH ₃ - NO	$-6.6258 \cdot 10^{-7}$	$5.7832 \cdot 10^{-9}$	$4.6281 \cdot 10^{-11} \ -1.9015 \cdot 10^{-14}$
$\rm NH_3$ - $\rm N_2O$	$-3.6194 \cdot 10^{-7}$	$1.8363 \cdot 10^{-9}$	$4.6399 \cdot 10^{-11} \ -2.1533 \cdot 10^{-14}$
NH ₃ - N ₂	$-6.6473 \cdot 10^{-7}$	$5.9607 \cdot 10^{-9}$	$4.5458 \cdot 10^{-11} \ -1.8455 \cdot 10^{-14}$
NH ₃ - H ₂	$-2.1379 \cdot 10^{-6}$	$1.3642 \cdot 10^{-8}$	$1.6957 \cdot 10^{-10} - 7.5904 \cdot 10^{-14}$
O ₂ - H ₂ O	$-2.5183 \cdot 10^{-7}$	$-4.5155 \cdot 10^{-11}$	$6.8874 \cdot 10^{-11} - 3.2829 \cdot 10^{-14}$
O ₂ - NO	$-5.7169 \cdot 10^{-7}$	$6.1153 \cdot 10^{-9}$	$3.6691 \cdot 10^{-11} - 1.3758 \cdot 10^{-14}$
O ₂ - N ₂ O	$-4.6322 \cdot 10^{-7}$	$3.7925 \cdot 10^{-9}$	$3.4369 \cdot 10^{-11} - 1.4500 \cdot 10^{-14}$
$O_2 - N_2$	$-5.6646 \cdot 10^{-7}$	$6.1869 \cdot 10^{-9}$	$3.6397 \cdot 10^{-11} - 1.3532 \cdot 10^{-14}$
O ₂ - H ₂	$-1.6020 \cdot 10^{-6}$	$2.0484 \cdot 10^{-8}$	$1.4360 \cdot 10^{-10} - 5.9717 \cdot 10^{-14}$
H ₂ O - NO	$1.1996 \cdot 10^{-7}$	$-3.2989 \cdot 10^{-9}$	$7.3440 \cdot 10^{-11} \ -3.4680 \cdot 10^{-14}$
$H_2O - N_2O$	$6.4485 \cdot 10^{-7}$	$-6.1589 \cdot 10^{-9}$	$6.0011 \cdot 10^{-11} - 2.1037 \cdot 10^{-14}$
H ₂ O - N ₂	$4.7898 \cdot 10^{-8}$	$-2.6903 \cdot 10^{-9}$	$7.2082 \cdot 10^{-11} \ -3.4244 \cdot 10^{-14}$
H ₂ O - H ₂	$-9.8748 \cdot 10^{-7}$	$2.2051 \cdot 10^{-9}$	$2.0524 \cdot 10^{-10} - 1.0683 \cdot 10^{-13}$
NO - N ₂ O	$-3.8180 \cdot 10^{-7}$	$2.4709 \cdot 10^{-8}$	$3.7548 \cdot 10^{-11} - 1.6929 \cdot 10^{-14}$
NO - N ₂	$-5.8581 \cdot 10^{-7}$	$5.6354 \cdot 10^{-9}$	$3.8441 \cdot 10^{-11} - 1.5112 \cdot 10^{-14}$
NO - H_2	$-1.5890 \cdot 10^{-6}$	$1.9980 \cdot 10^{-8}$	$1.4192 \cdot 10^{-10} - 5.8594 \cdot 10^{-14}$
N ₂ O - N ₂	$-4.0237 \cdot 10^{-7}$	$2.7453 \cdot 10^{-9}$	$3.7073 \cdot 10^{-11} - 1.6537 \cdot 10^{-14}$
$N_2O - H_2$	$-1.8960 \cdot 10^{-6}$	$1.8279 \cdot 10^{-8}$	$1.1329 \cdot 10^{-10} - 3.8471 \cdot 10^{-14}$
N ₂ - H ₂	$-1.6373 \cdot 10^{-6}$	$2.1403 \cdot 10^{-8}$	$1.2959 \cdot 10^{-10} - 5.2052 \cdot 10^{-14}$

Table A.4.: Polynomial coefficients for the temperature-dependent binary diffusion coefficients.

()
$e \ / \ m^2 \ s^{-1} \ K^{-4} f \ / \ m^2 \ s^{-1} \ K^{-5}$
$6.5090 \cdot 10^{-18} \ -1.1508 \cdot 10^{-21}$
$1.3066 \cdot 10^{-16} \ -3.5470 \cdot 10^{-20}$
$7.5597 \cdot 10^{-18} \ -1.3533 \cdot 10^{-21}$
$8.8182 \cdot 10^{-18} \ -1.5920 \cdot 10^{-21}$
$7.3055 \cdot 10^{-18} \ -1.3051 \cdot 10^{-21}$
$3.2181 \cdot 10^{-17} \ -6.1431 \cdot 10^{-17}$
$1.3372 \cdot 10^{-17} - 2.3967 \cdot 10^{-21}$
$5.2697 \cdot 10^{-18} \ -9.2540 \cdot 10^{-22}$
$5.8163 \cdot 10^{-18} \ -1.0452 \cdot 10^{-21}$
$5.1623 \cdot 10^{-18} \ -9.0449 \cdot 10^{-22}$
$2.4183 \cdot 10^{-17} \ -4.3524 \cdot 10^{-21}$
$1.3700 \cdot 10^{-17} - 2.3874 \cdot 10^{-21}$
$6.1958\cdot 10^{-18}\ -8.1778\cdot 10^{-22}$
$1.3639 \cdot 10^{-17} \ -2.3930 \cdot 10^{-21}$
$4.7674 \cdot 10^{-17} \ -9.2082 \cdot 10^{-21}$
$6.9080\cdot 10^{-18} \ -1.2483\cdot 10^{-21}$
$5.9083 \cdot 10^{-18} \ -1.0490 \cdot 10^{-21}$
$2.3429 \cdot 10^{-17} \ -4.1629 \cdot 10^{-21}$
$6.7339 \cdot 10^{-18} \ -1.2164 \cdot 10^{-21}$
$1.2651 \cdot 10^{-17} \ -1.8838 \cdot 10^{-21}$
$2.1345\cdot 10^{-17} \ -3.9418\cdot 10^{-21}$

Table A.4.: (Continued)

B. Estimation of O₂ and NO near-surface concentrations

One major result of this work is that local variations in the N₂O selectivity as well as the response of the selectivity to changes in the flow velocity and gauze geometry are mainly caused by changes in the local near-wall NH₃ concentration. This argument is based on the observation, that the near-surface concentrations of the other reactants NO and O₂ show little variation across local entities of the gauze and weak dependency on the operating conditions. In the following section, based on the concept of mass transfer coefficients, analytic expressions for the gas phase concentrations of O₂ and NO near the catalyst surface will be derived. These equations reveal that the near-surface concentrations are only determined by the stoichiometry of the overall reaction and the intensity of O₂ and NO mass transfer relative to the mass transfer of NH₃. Thus the dominating role of the local NH₃ concentration is not a feature of the chosen mechanistic model but should be present using any mechanism, given that the overall reaction is controlled by NH₃ mass transfer.

Assuming that the reaction is in the mass transfer controlled regime, the ammonia concentrations near the surface of the catalyst are small compared to the bulk concentrations and the molar flux of ammonia to the catalyst wire is given by:

$$J_{\rm NH_3} = \beta_{\rm NH_3} c_{\rm film} \left(x_{\rm b, NH_3} - x_{\rm s, NH_3} \right) \approx \beta_{\rm NH_3} c_{\rm film} x_{\rm b, NH_3} \tag{B.1}$$

 $c_{\rm film}$ is the molar density of the film, $x_{\rm b,NH_3}$ the ammonia bulk mole fraction in contact with the particular point on the gauze surface, $x_{\rm s,NH_3}$ the ammonia mole fraction near the gauze surface and $\beta_{\rm NH_3}$ the corresponding mass transfer coefficient. In steady state, the flux of O₂ to the catalyst surface must then equal the flux of NH₃, taking into account the stoichiometry of reaction R1:

$$\beta_{O_2} c_{\text{film}} \left(x_{\text{b},O_2} - x_{\text{s},O_2} \right) = \nu \,\beta_{\text{NH}_3} \,c_{\text{film}} \,x_{\text{b},\text{NH}_3} \tag{B.2}$$

Here ν denotes the ratio of the stoichiometric coefficients of NH₃ and O₂ in reaction (R1) and is equal to 5/4. Rearranging for x_{s,O_2} and replacing the mass transfer coefficients by the respective Sherwood numbers (*Sh*), we obtain the following expression:

$$x_{\rm s,O_2} = x_{\rm b,O_2} - \nu \, \frac{Sh_{\rm NH_3} \, D_{\rm NH_3}}{Sh_{\rm O_2} \, D_{\rm O_2}} \, x_{\rm b,NH_3} \tag{B.3}$$

Sh is typically a function of the Reynolds number (Re) and the Schmidt number (Sc). For mass transfer from a wire, common correlations suggest the following expression for Sh of a species *i*:

$$Sh_i = f(Re) \cdot Sc_i^{1/3}$$
 with $Sc_i = \frac{\mu}{\rho D_i}$ (B.4)

Plugging Equation (B.4) into Equation (B.3) yields the final expression for the near-surface mole fraction:

$$x_{\rm s,O_2} = x_{\rm b,O_2} - \nu \left(\frac{D_{\rm NH_3}}{D_{\rm O_2}}\right)^{2/3} x_{\rm b,NH_3}$$
(B.5)

Following the same procedure, a similar expression for the near surface mole fraction of NO is obtained:

$$x_{\rm s,NO} = x_{\rm b,NO} + \nu \left(\frac{D_{\rm NH_3}}{D_{\rm NO}}\right)^{2/3} x_{\rm b,NH_3}$$
 (B.6)

According to reaction R1, $\nu = 1$ in Equation (B.6). In both equations, the near surface mole fractions depend on the stoichiometry of the overall reaction and the ratio between the diffusion coefficients of ammonia and O₂ or NO respectively. No specific details of the surface kinetics are contained within these expressions. One should however be aware that for the derivation of Equations (B.5) and (B.6) it was assumed that the overall reaction proceeds with a NO selectivity of 100%. Since product selectivity depends on the chosen kinetic model, there is indeed an influence of the details of the reaction kinetics on the concentrations near the catalyst surface. Recalling that for industrial ammonia oxidation the NO selectivity is significantly higher than the selectivities towards N₂O and N₂, the effect on the concentrations however is rather small. To evaluate in how far the equations above are suited to assess the near surface concentrations of O₂ and NO, the concentrations obtained by Equations (B.5) and (B.6) are compared to the concentrations at the tip of the single wire from the CFD simulations in section 5.3.2. The diffusion coefficients are evaluated at the film conditions in front of the wire tip according to Equation (5.18). As can be seen from the results in Table B.1 the estimated concentrations agree quite well with the simulation results.

When discussing the deviations between the estimated and simulated concentrations, one has to be aware of the fact that the overall reaction does not proceed with an NO selectivity of 100%, which was assumed when deriving Equations (B.5) and (B.6). Furthermore the evaluation of the diffusion coefficients at film conditions is another approximation. Lastly, Equations (B.5) and (B.6) are only valid for an entirely mass transfer controlled reaction. Although the NH_3 oxidation reaction in the CFD model is governed by external mass transfer, it does not fully lie in the mass transfer limited regime as demonstrated in section 5.4.5.

Table B.1.: Near surface concentrations of O ₂ and NO at the tip of the wire estimated via Equations	(B.5) an	d
(B.6) and from the single wire simulation with standard conditions of Table 5.2.		

	Estimate	Simulation
c_{O_2} / mol m ⁻³	3.05	3.16
$c_{\rm NO}$ / mol m ⁻³	5.58	5.25

C. Strategy for calculating the sensitivity matrix

This chapter presents an approach to calculate $J_{\theta,k}$ by the solution of the analytic Equation (C.1).

$$\boldsymbol{J}_{\boldsymbol{\theta},\boldsymbol{k}} = -\boldsymbol{J}_{\boldsymbol{\dot{\theta}},\boldsymbol{k}} \left(\boldsymbol{J}_{\boldsymbol{\dot{\theta}},\boldsymbol{\theta}} \right)^{-1} \tag{C.1}$$

As outlined in section 6.3.3.2, $J_{\dot{\theta},\theta}$ is a singular matrix and thus not directly invertible. To solve Equation (C.1) the following procedure was used:

Suppose the kinetic model suggests only one type of adsorption site and the index of this surface site species is nS (highest index occurring in $J_{\dot{\theta},\theta}$). To make the matrix invertible, the last entry of every row is subtracted from all other entries of the row and then the size of the matrix is reduced by removing the last row as well as the last column, i.e. removing all entries involving the free surface site:

$$J_{\dot{\theta},\theta,i,j}^{\text{red}} = J_{\dot{\theta},\theta,i,j} - J_{\dot{\theta},\theta,i,nS} \qquad \text{for } i, j = 1, \dots, nS - 1$$
(C.2)

This removes the linear dependent row from the matrix (which arise from the fact, that the sum of all surface coverages θ is equal to one. In its reduced form $J_{\dot{\theta},\theta}^{\text{red}}$, the matrix is now invertible. In order to obtain $J_{\dot{\theta},\theta}$, a few additional steps are required. To perform a matrix multiplication, the dimensions of the matrices must match and thus the last row of $J_{\dot{\theta},k}$ also needs to be removed.

$$J_{\dot{\theta},k,i,j}^{\text{red}} = J_{\dot{\theta},k,i,j} \qquad \qquad \text{for } j = 1, \dots, nS - 1 \quad (C.3)$$

The reduced form of $J_{\theta,k}$ is then given by:

$$J_{\theta,k}^{\text{red}} = -J_{\dot{\theta},k}^{\text{red}} \left(J_{\dot{\theta},\theta}^{\text{red}}\right)^{-1}$$
(C.4)

The full matrix is obtained by adding a row to the bottom, which is given by the negative sum of all other rows:

$$J_{\theta,k,i,j} = J_{\theta,k,i,j}^{\text{red}} \qquad \text{for } j = 1, \dots, nS - 1$$
$$J_{\theta,k,i,nS} = \sum_{j}^{nS-1} - J_{\theta,k,i,j}^{\text{red}} \qquad (C.5)$$

The steps described above can also be applied to surface kinetic models with more than one type of adsorption site. Please note that the procedure of adding and removing rows and columns must then be performed for every different type of surface site.

D. Degree of rate control of the optimized microkinetic model

	$\rm NH_3$	0 ₂	H ₂ O	NO	N ₂ O	N_2	H ₂
R1	1.4279	1.3103	1.4279	1.0940	2.8296	4.7488	2.5212
R2	-0.4412	-0.3463	-0.4412	-0.1665	-1.9872	-3.0613	-2.6749
R3	0.0001	0.0001	0.0000	0.0001	-0.0001	-0.0003	-0.0028
R4	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000
R5	0.0023	0.0021	0.0023	0.0018	0.0046	0.0078	0.0413
R6	-0.0000	-0.0000	-0.0000	-0.0000	0.0000	0.0002	0.0016
R7	-0.0011	-0.0013	-0.0011	-0.0017	0.0015	0.0051	0.0486
R8	0.0000	0.0000	0.0000	0.0000	-0.0000	-0.0000	-0.0004
R9	0.0000	0.0001	0.0000	0.0001	-0.0000	-0.0002	-0.0018
R10	0.0011	0.0013	0.0011	0.0017	-0.0016	-0.0052	-0.0504
R11	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0004
R12	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0002
R13	-0.0000	-0.0000	-0.0000	-0.0000	0.0000	0.0001	0.0019
R14	-0.0000	-0.0000	-0.0000	-0.0001	0.0000	0.0001	-0.0173
R15	-0.0015	-0.0018	-0.0015	-0.0024	0.0022	0.0074	0.0706
R16	-0.0004	-0.0004	-0.0004	-0.0006	0.0005	0.0017	0.0331
R17	0.0263	0.0786	0.0263	0.1763	-0.6998	-1.4384	0.1535
R18	0.0006	0.0008	0.0006	-0.0010	-0.0029	-0.0030	-0.0006
R19	-0.0123	-0.0378	-0.0123	-0.0793	-0.1281	0.7670	-0.0755
R20	-0.0018	-0.0056	-0.0018	-0.0245	0.9870	-0.0312	-0.0111
R21	-0.0000	-0.0001	-0.0000	-0.0000	-0.0139	0.0040	-0.0002
R22	0.0000	0.0001	0.0000	0.0000	0.0080	-0.0021	0.0001

Table D.1.: Full $X_{\rm RC}$ of the optimized microkinetic model, originally published by Traversac.

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