Local investigations of catalysts at work: An insight into a catalytic reactor

Jespersen, Sebastian Pirel Fredsgaard

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LOCAL INVESTIGATIONS OF CATALYSTS AT WORK

An insight into a catalytic reactor

SEBASTIAN PIREL F. JESPERSEN

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An insight into a catalytic reactor

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SUPERVISORS:
Associate Professor:
Christian Danvd Damsgaard
DTU Physics and DTU Nanolab

Fellow:
Stig Helveg
Haldor Topsoe A/S
This thesis is submitted in the candidacy of the PhD degree from the Technical University of Denmark (DTU). The thesis was prepared with funding from Haldor Topsoe A/S and DTU Physics. I gratefully acknowledge their support. The work presented herein was performed from June 2016 to July 2019 under the supervision of fellow Stig Helveg and associate professor Christian Danvad Damsgaard.

I would like to start by showing my gratitude to my supervisor from DTU, Christian Danvad Damsgaard, who introduced me to the field of electron microscopy already at my second year as undergraduate student. Since then, Christian D. Damsgaard has supervised me through my bachelor, my master and finally my PhD. For that I am very thankful.

I would also like to show my gratitude to my supervisor from Haldor Topsoe A/S, Stig Helveg, for inviting me into the in situ TEM group at Haldor Topsoe A/S. It has been most exciting to experience the scientific environment in the Atomic-Scale Analysis Department at Haldor Topsoe. I have learned a tremendous amount in the last four years. I am very grateful.

I would like to dedicate this thesis to my dad who unfortunately passed away in November, 2015. Since the time in lower secondary school, where I was told that I wasn’t fit for an academic education due to my dyslexia, I have been fighting doggedly to prove them wrong. During this life long process, my dad has always been a true support and a rock for me. As he had dealt with similar problems with dyslexia in his life, he was able to guide me and provided me with useful tools to overcome my difficulties in ways that other weren’t able to. To this day, his repeated saying is still melted into my DNA, declaring that; “as long you perform your best, nobody can ask for more!” I can proudly say that I have done my best, and the result is collected within this thesis. I truly hope you will enjoy reading it.

Kgs. Lyngby, June 2019

Sebastian Pirel F. Jespersen
ABSTRACT

Heterogeneous catalysis, where gas reactants chemically react on the surface of a catalyst, have had and still have a tremendous impact on humanity and the modern world. Without heterogeneous catalysis, the inhabitants of the world could not be fed and the estimated world population would only count 3.5 billion people, corresponding to half of the number of today. It is estimated that about 90% of all chemicals produced today have undergone a catalytic process, including the production of plastics, polymers and fuels. In general, the world has become a better place. However, a growing population and increasing living standards world-wide have led to new demands of natural resources and new world problems, climate changes included, which need to be solved. Here, heterogeneous catalysis is going to play a major role in finding sustainable solutions.

The secret to the catalytic ability of the catalyst lies within the atomic configuration of the surface terminations. The key to developing new efficient and effective catalysts are hence to fully understand the relation between the atomic configuration of the catalyst surfaces and their activity.

Transmission electron microscopy has the capability to visualize the nano-structure of the catalysts with a resolution on the atomic-scale and can thus reveal insight of the atomic configurations. In this thesis, transmission electron microscopy is used to investigate the dynamics of catalysts. To do this, nano-scale reactors based on Silicon technology were employed to simulate the conditions found in real chemical reactors. These so-called nanoreactors allow the catalyst loaded in the reactor to be studied at a pressure of several bars and elevated temperatures. Such in situ studies are of utmost importance because the gas composition, the pressure and the temperature are all known to influence the catalyst structure.

The thesis will address four topics, all related to the use of transmission electron microscopy and the nanoreactor with the perspective of visualizing the catalyst under its active state.

The first topic will seek to address the limit for the attainable resolution while introducing gas to the nanoreactors. As the gas pressure increases in the reactor, the number of interactions between the electrons and gas molecules will rise, which will lead to a degradation of the resolution. Studies have, however, indicated how tuning of the electron beam can postpone the degradation to higher pressure levels. This topic will therefore address how the properties of the electron beam, the pressure as well as the gas type, affect the inher-
ent resolution of the microscope while employing the nanoreactor system.

The second topic will report on the integrity of the Silicon-based electron-transparent windows of the nanoreactor. Transmission electron microscopy can become destructive and manipulative if one is not fully aware of controlling the electron beam probably. How the electron beam affects the specimen depends strongly on the specimen itself, the operational conditions and the illumination conditions. The investigation will therefore study how the operational conditions (pressure and temperature) and the illumination conditions (primary electron energy and the electron dose rate) influence the nanoreactor integrity while exposed to an oxidizing environment.

The third topic will address the catalytic oxidation of CO over Pt nanoparticles. The catalytic system is used to address how the local environment along the reactor varies from the overall conversion for the entire reactor, and how the local particle shapes relate to the local environment in which they sit compared to the global activity. To do so, electron energy-loss spectroscopy is utilized to probe the local environment, whereas mass spectroscopy is used to integrate over the entire reactor.

Lastly, topic four will address an industrial-style Cu/ZnO catalyst used for methanol synthesis. Here, the structure dynamics of the catalyst is investigated under high pressure conditions. During this examination it will become clear how important it is to be fully aware of the electron beam and to control it.

With these four topics, it will, hopefully, be transparent why transmission electron microscopy in combination with the nanoreactor system is a powerful tool in the research for understanding and developing new, efficient and effective catalysts to help solve the problems of today.

Hemmeligheden bag katalysatorens katalytiske evner skal findes i den atomare konfiguration af katalysatorens overflade. Nøglen til at udvikle nye effektive og økonomiske katalysatorer, er derfor at forstå forholdet mellem den atomare konfiguration af katalysatorens overflader, og deres aktiviteter til fulde.

Transmission elektron mikroskopi giver mulighed for at visualisere nano-strukturen af katalysatorer med en oplosning på atomar skala, og kan derved give indsigt i den atomare konfiguration af katalysatorens overflade. I denne afhandling vil transmissions elektron mikroskopi benyttes til at undersøge dynamikken af katalysatorer. Dette er gjort ved at benytte nano-størrelse reaktorer, baseret på silicium teknologi, til at simulere forholdene som findes i industrielle kemiske reaktorer. Disse såkaldte nano-reaktorer muliggør at studere katalysatorer i reaktoren ved betingelser som op til flere bars tryk samt under opvarmning. Sådanne in situ studier er af allervigtigste betydning, da det er kendt at katalysatorens struktur afhænger af gassammensætningen, trykket og temperaturen.

Denne afhandling vil adressere fire emner som alle omhandler brugen af transmission elektron mikroskopi i kombination med nano-reaktoren med henblik på at visualisere katalysatorer under deres aktive stadie.

Det første emne forsøger at afdække hvad den opnåelige oplosningsgrænse er for nano-reaktoren i reaktoren men henblik på at visualisere katalysatorer under deres aktive stadie. Gastrækket i en reaktor bliver øget, vil antallet af interaktioner mellem elektronerne og gas- molekylerne stige, hvilket vil medføre en degradering af oplosningen. Studier har dog påvist at man, ved at justere elektronstrålenes egenskaber kan udskyde degraderingen til højere tryk. Dette emne vil derfor adressere, hvorledes egenskaberne
af elektronstrålen, trykket, samt typen af gas påvirker den iboende opløsning af mikroskopet, ved benyttelse af nano-reaktor systemet.


Tredje emne vil adressere den katalytiske oxidation af kulstofmonoxid over platin nano-partikler. Det katalytiske system er benyttet til at adressere, hvorledes det lokale miljø ned igennem nano-reaktoren varierer fra den overordnede konvertering fra hele reaktoren og hvordan den lokale partikelform relaterer til det lokale miljø i hvilket partiklerne er placeret, frem for den globale aktivitet. For at realisere dette, er elektron energitabs spektroskopi benyttet til at afdække det lokale miljø, hvorimod at masse spektroskopi er benyttet til at integre over hele reaktoren.

Til sidst vil det fjerde emne belyse en industriel lignende kobber zincoxid katalysator brugt til metanol syntese. Her vil katalysatorens struktur dynamik blive undersøgt under højt tryk. Igennem eksamination vil det blive klargjort, hvor vigtigt det er at have fuldt styr på elektronstrålen og at kontrollere den korrekt.

Med disse fire emner vil det forhåbentlig stå klart, hvorfor transmission elektron mikroskopi i samarbejde med nano-reaktor systemet er et vigtigt redskab i søgen efter nye effektive og økonomiske katalysatorer til at hjælpe med at løse vore dages store problemer.
PUBLICATIONS

PAPER A

On the integrity of MEMS-based window cells in TEM experiments
Sebastian Pirel F. Jespersen, Hjalte Rørbech, Peter C. K. Vesborg, Christian D. Damsgaard, and Stig Helveg
In preparation (2019)

PAPER B

Effects of local environment for the shape and activity of a Pt catalyst during CO oxidation
Christian F. Elkjær, Sebastian Pirel F. Jespersen, Søren B. Vendelbo, Patricia Kooymann, Christian D. Damsgaard, Ib Chorkendorff, and Stig Helveg
In preparation (2019)

PAPER C

Influence of electron-dose-rate, gas environment, and specimen on the image resolution in ambient pressure transmission electron microscopy
Sebastian Pirel F. Jespersen, Bas Hendriksen, Luigi Mele, Pluen Dona, Joerg Jinschek, Christian D. Damsgaard, and Stig Helveg
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PAPER D

Reversibility between Platinum single atoms and nano-culsters and its effect on reactivity for propylene oxidation
Debasish Chakraborty, Thomas E. L. Smithhusen, Sebastian Pirel F. Jespersen, Arvin Kakekhani, Hugo Silva, Christian D. Damsgaard, Ib Chorkendorff, and Stig Helveg
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<td>contrast transfer function</td>
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<tr>
<td>CCD</td>
<td>charged coupled device</td>
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<td>field emission gun</td>
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<td>Gatan image filter</td>
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<td>FWHM</td>
<td>full width half-maximum</td>
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<td>HRTEM</td>
<td>high-resolution transmission electron microscopy</td>
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<td>IGP</td>
<td>ion getter pump</td>
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<td>low-loss</td>
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<tr>
<td>SEM</td>
<td>secondary electron multiplier</td>
</tr>
<tr>
<td>STEM</td>
<td>scanning electron microscopy</td>
</tr>
<tr>
<td>SNR</td>
<td>signal-to-noise ratio</td>
</tr>
<tr>
<td>TEM</td>
<td>transmission electron microscopy</td>
</tr>
<tr>
<td>TOF</td>
<td>turnover frequency</td>
</tr>
<tr>
<td>TMP</td>
<td>turbo-molecular pump</td>
</tr>
<tr>
<td>VEELS</td>
<td>valence electron energy-loss spectroscopy</td>
</tr>
<tr>
<td>WPOA</td>
<td>weak phase object approximation</td>
</tr>
<tr>
<td>ZLP</td>
<td>zero loss peak</td>
</tr>
</tbody>
</table>
INTRODUCTION

This chapter serves as an introduction to the field of catalysis and the research presented in this thesis. First, an overview which presents some of the fundamental challenges of humanity, where catalysis can be the solution. Electron microscopy is motivated as a useful tool in the development of such solutions. Finally, an overview of the thesis structure is provided together with a brief introduction to each of the research topics.
1.1 A WORLD OF CONSUMERS

On the newscast at the Danish Radio on August the 1st, 2018, it sounded that the Earth Overshoot Day was attained. That is the date that marks when humanity’s ecological resource consumption for the year exceeds what the Earth is capable of regenerating in that year [1]. It is the Global Footprint Network that every year estimates this date by computing the Earth’s biocapacity (the amount of natural resource regenerated by Earth in a year) divided by humanity’s ecological footprint (humanity’s consumption of natural resources that year) times the number of days in the year.

Earth Overshoot Day:
\[
\frac{\text{Earth’s biocapacity}}{\text{Humanity’s ecological footprint}} \times 365 \text{ days}
\]

Earth’s biocapacity: the amount of natural resources that Earth can regenerate per year.

Humanity’s ecological footprint: humanity’s consumption of natural resources per year.

It is alerting that the date is arriving earlier every single year, as illustrated by Figure 1, which demonstrates the dates for the Earth Overshoot Day since 1970. Figure 1 also displays the yearly ecological consumption and the Earth’s biocapacity, showing a general rapid increase in consumption, whereas the biocapacity lags behind. However, since 2010 the Earth Overshoot Day seems to be stagnant around the first week of August, which leaves humanity’s resource consumption at a level that equates 1.7 times the Earth’s biocapacity.
Figure 1: Earth Overshoot Day, the ecological resource consumption and the Earth biocapacity since 1970. The Earth Overshoot Day is determined as the date where the humanity’s ecological resource consumption (depicted as the red line) for the year exceeds what Earth is able to regenerate (depicted as the green line) in that same year. The data is adopted from National Footprint Accounts 2019 [1].

It is even more alerting when consulting the Overshoot Day for each individual country, as illustrated in Figure 2. The Country Overshoot Day is based on the average ecological consumption per person for the given country compared to the global biocapacity per person. Here, the top consumers are countries, which could be considered as the western world, together with countries rich on oil, such as Qatar and the United Arab Emirates. For those countries, their overshoot day is dated within the first half of the year, i.e. meaning before July 1st.

To sustain the resources of Earth, the global ecological footprint has to be reduced to a level as in the 1970s or put in another perspective, at a level similar to what they have in Indonesia. However, it is unlikely that humanity will give up their current standard of living to decrease the global ecological consumption. Moreover, countries as Indonesia, which are ranking low in the Country Overshoot Days chart, will most likely increase there yearly ecological consumption as to reach similar living standards as countries that are ranking high in Figure 2. As an example of this, Vietnam was estimated to a Country Overshoot Day dated of December 21st in 2018, where this year Vietnam is estimated to October 18th, 2019 [1]. The same tendency is current for Columbia, Thailand, and Costa Rica, to mention some [1]. Therefore, a more pragmatic solution might be to increase the Earth biocapacity, if achievable, or to harness the resources as efficiently as possible.
Figure 2: Estimate of Earth Overshoot Day for each countries in 2019. The estimation is based on data from 2016 and is computed as the average natural resource consumption per person for the given county in relation to the global biocapacity per person. The figure is adopted from National Footprint Accounts 2019 [1] and modified.

1.2 THE IMPACT OF CATALYSIS ON HUMANITY

Humanity has earlier faced challenges in terms of attaining resources. At the entrance to the 20th century, the production of ammonia was among the most significant productions at its time. The reason for this was that ammonia was used to provide Europe with fertilizer to prevent a famine. However, fertilizer was a scarce resource, and the food production was inhibited in many parts of the world.

In 1903, during their work at BASF, Fritz Haber and Walther Nernst discovered that the activity and the equilibrium concentration in the ammonia production could be improved, if pressure and temperature were raised. The process was further improved in 1905, where Haber introduced an iron-based material, known as a catalyst. During the next 4 years, Haber together with co-workers Carl Bosch and Poul Alwin Mittasch continued the development on the ammonia process, resulting in the first industrial catalyst for the production of ammonia from hydrogen and nitrogen, which was launched in 1909 [2].

Today, the process is known as the Haber-Bosch process, and in a 1999 essay published by the Nature Magazine it was argued to be the most important scientific discovery of the 20th century [3]. It is because of the Haber-Bosch ammonia process that Earth can sustain the still growing world population [3, 4]. At the entrance of the 20th century, the world population was around 1.5 billion people, as shown in Figure 3. As the industrial process of synthesizing ammonia be-
1.3 THE WORKING PRINCIPLE OF CATALYSIS

Catalysis is the phenomenon of accelerating the rate of a reaction, by introducing a material (the catalysts) into the reaction \[5\]. Here, the catalysts increase the speed of reaction without being consumed in the reaction itself. In that sense, the catalyst helps a reaction to occur while consuming less energy than usual (i.e. without the catalyst). Besides making a reaction more favorable, a suitable catalyst also avoids unwanted bi-product to be formed by being selective towards a specific product. In a compact manner, the term catalyst can be defined as:

**Catalyst:**
A substance that accelerates the rate of a reaction towards its thermodynamic equilibrium without being consumed in the process or modifying the overall standard Gibbs energy change in the reaction.

Catalysts can be divided into three different categories; heterogeneous catalysts, homogeneous catalysts, and biocatalysts. Starting

---

Figure 3: Impact of Haber-Bosch process on the world population The chart displays the growth of the world population since 1900, together with the percentages of the population who are fed by use of the Haber-Bosch process. Without the Haber-Bosch ammonia process, Earth could not sustain more than around 3.5 billion people. Reproduction of [4].

In 1910, the world population has been drastically increased over the years, and today the world population surpassed 7.5 billion. It is estimated that almost 50% of the world population today is fed by fertilizer produced from the Haber-Bosch ammonia process[4]. That is only possible thanks to catalysis.
with the latter, biocatalysts are probably the most commonly known to the non-scientific community, as these are enzymes. Enzymes are protein-chains that our body produces to help with decomposing food to energy or to kill bacteria and viruses. Also in industry, enzymes play a significant role where they are used to prolong the lifespan of food or help to clean the laundry and dishes, just to mention some few examples. Homogeneous catalysts are, as the name suggests, where the catalyst is in the same phase as the reactions (e.g. liquid). Finally, we have heterogeneous catalysts where the catalysts and the reactants are in separate phases, often in a phase of solid metals or metal-oxides for the catalyst and gas for the reactants.

In this thesis, only heterogeneous catalysis has been studied, where the catalysts are in forms of solid metal nanoparticles and the reactants, as well as the products, are different gas compounds. Therefore, an example from the field of heterogeneous catalysis, the oxidation of CO, is here used to go a bit deeper into the understanding of catalysis. The CO oxidation is a key reaction in cleaning automotive exhaust and is, as it will be shown later, an essential part of this thesis. The reaction is catalyzed on a surface of a noble metal such as platinum, Pt.

In CO oxidation, carbon monoxide, CO, and oxygen, O\textsubscript{2}, (the reactants) react to form carbon dioxide, CO\textsubscript{2}, (the product). For the reaction to be stoichiometric, i.e. meaning that the total mass of the reactants equals the total mass of the products, two CO molecules is needed for each O\textsubscript{2} molecule present to form two CO\textsubscript{2} molecules.

\[
2 \text{CO} + \text{O}_2 \rightarrow 2 \text{CO}_2 \quad \text{(Stoichiometric)}
\] (1)

In Figure 4, a sketch of the potential energy diagram for CO oxidation is displayed, comparing the non-catalyzed and catalyzed pathway for the reaction. If the reactants have to react in a non-catalyzed way, the reactants first have to collide with each other where they have to break their chemical bonds for them to create new bonds and form the CO\textsubscript{2}. To do so, the reactants have to overcome a larger energy barrier, known as the activation energy, which is illustrated by the dashed line in Figure 4.

By introducing a catalyst, an alternative pathway for the reaction is provided. The catalyst does so by providing a surface consisting of active sites (denoted as *) with which the reactants form bonds. This brings them into a configuration where it becomes more favorable to react towards the product. The alternative pathway may be more complex, but the activation energy of each step is significantly lower than that of the uncatalyzed reaction. Figure 4 displays this alternative pathway together with each step’s activation energy, illustrated by the solid lines.
Breaking down the catalytic pathway, the reaction transits through a number of elementary steps. First, the reacting molecules are adsorbed to the surface of the catalyst. At the surface, the \( \text{O}_2 \) molecule breaks up (dissociates) into two \( \text{O} \) atoms. We can denote these two first steps formally as

\[
\text{O}_2 + 2 \, \text{\textdegree} \, \text{\textstar} \rightleftharpoons 2 \, \text{\textstar} \left( \text{2} \right)
\]

\[
\text{CO} + \, \text{\textstar} \rightleftharpoons \text{CO} \, \text{\textstar} \left( \text{3} \right)
\]

where \( \text{\textstar} \) indicate that the atom/molecule has bound to the surface site \( \text{\textstar} \). The adsorbed \( \text{O} \) atom and the adsorbed \( \text{CO} \) molecule starts diffusing around on the surface of the catalyst until the two species meet and react to form \( \text{CO}_2 \). The created product, \( \text{CO}_2 \), is very stable and, therefore, only interacts weakly with the catalyst surface. Consequently, the \( \text{CO}_2 \) molecule will almost instantaneously desorb from the surface (i.e. break free and leave the surface).

\[
\text{CO} \, \text{\textstar} + \text{O} \, \text{\textstar} \rightleftharpoons \text{CO}_2 + 2 \, \text{\textstar} \left( \text{4} \right)
\]

The desorption of the \( \text{CO}_2 \) molecule will liberate the two active sites on which the \( \text{CO} \) and \( \text{O} \) were bound. This leaves the active sites available for new reaction cycles. Thus, how much \( \text{CO} \) the catalyst can oxidized becomes limited by the number of active sites available and, therefore, a question of how fast the \( \text{CO}_2 \) desorbs from the surface. Hence, the expression \textit{turnover frequency} (\textit{TOF}) is often used to
describe how active a given catalyst is, telling how many reaction events occur per active site per unit time.

1.4 INDUSTRIAL CATALYTIC PRODUCTIONS

Roughly 90% of all chemical products today are produced by industrial catalytic processes [5]. Among those are processes such as synthesis of ammonia or methanol (MeOH), or hydrotreatment of crude oil, which all take place in large scale chemical plants, producing thousand of tons of products every single day. Where ammonia is used in the fertilizer industry, methanol is used as a raw material in the production of many difference chemicals, such as formaldehyde, polymers and higher alcohols. Hydrocracking is the process of splitting (cracking) the longer hydrocarbon-chains of the crude oil into smaller chains, from which products as gasoline and diesel are produced.

Without the use of industrial catalysts, many of these industrial processes would not be possible nor economically feasible. Optimizing the catalysts results in reduction of energy and operational costs. Often, catalytic routes can be designed such that raw materials are used efficiently and waste production is minimized [5]. Every single day, scientists around the world dedicate their work life to improve and perfect industrial catalysts, such that Earth’s resources are harnessed to the best of its capabilities. By use of kinematic modelling, computer simulation, theoretical calculations, experiments and characterisation, the scientists try to achieve knowledge about the catalytic reactions such to understand the phenomena down to an atomic level. Ideally, the scientists desire the possibility to look into an operating catalytic reactor and visualizes the catalytic reaction as it occurs, and eventually see the catalyst at work.

Today, this desire is almost met, as the atomic structures of a catalyst can be visualized by use of electron microscopy with a resolving power around 1 Å (being one tenth of a million of a mm). Contemporarily, it has become possible to employ nanometer-scale reactors into the microscopes, which can simulate real conditions for the catalytic reaction. These advantages have been utilized in this thesis and is the subject of the thesis.

1.5 THESIS STRUCTURE

In this thesis, it will be demonstrated how TEM can be facilitated to visualize the catalyst at work and to measure the activity of an ensemble of catalysts. This is done by simulating real reaction conditions by utilizing a nanometer-scale reactor, which fits into the microscope. The thesis will highlight the advantages of such a reactor, but also evaluates on its difficulties and limitations.
The list below provides an overview of the thesis structure together with a short description of the chapter contents.

**CHAPTER 2** introduces the relevant methodology for understanding this thesis.

**CHAPTER 3** explores the resolution limit for TEM studies as gas is introduced to the microscope. Here, a comparison of the differentially pumped system and the closed window cell, the so-called nanoreactor, is provided, demonstrating significant difference between the two systems.

**CHAPTER 4** reports on the integrity of the nanoreactor during oxidizing reaction conditions. The chapter addresses on the influence of the operational as well as the illumination conditions on the integrity.

**CHAPTER 5** challenges the common way to relate the structure and functionality of the catalyst. The chapter delivers a direct comparison between a local probing and a global integral of the catalytic activity and related it to catalyst structure dynamics.

**CHAPTER 6** investigates on the structural dynamics of an industrial-style methanol catalyst while operated under high pressure. The chapter will clarify why control and awareness of the electron beam properties are so vital while working with electron microscopy.
METHODOLOGY

The chapter will present the methodologies that are employed throughout the thesis. Herein, transmission electron microscopy (TEM) will be described in detail together with the working principle of in situ experiments, including the use of the differentially pumped system and the closed window cells. Moreover, the chapter will address the use of mass spectrometer (MS) and electron energy-loss spectroscopy (EELS).
2.1 TRANSMISSION ELECTRON MICROSCOPY

Experiments presented in this PhD thesis have been performed using TEM. TEM is a microscopy technique that relies on highly energetic electrons, which are transmitted through a specimen and used to visualize the specimen. This sets some requirements to the specimen, which will be addressed later. The TEM is equivalent to light optical microscopy (LOM), as both techniques form a two-dimensional image of a three-dimensional object, i.e. the specimen. Where LOM uses photons as its probe, TEM uses electrons, which is why TEM performs significantly better in terms of resolution.

Resolution

Resolution refers to the smallest possible structure or object that the microscope can resolve. Consequently, smaller resolvable structures mean higher resolution.

The resolution is determined by the wavelength of the probe, i.e. meaning that the smaller the wavelength is, the better the resolution becomes. For light in the visible spectrum, the wavelength lies in the regime of 400 nm to 700 nm, resulting in a resolution limit around 300 nm in consequence of the Rayleigh criterion [6]. Unfortunately, for many scientific aspects, this maximum resolution of 300 nm is insufficient. Luckily, due to the particle-wave duality, the wavelength of an electron is related to its momentum $p$ and is described by the de Broglie equation [6]:

$$\lambda = \frac{h}{p} \quad (5)$$

where $h$ denotes the Planck constant. The momentum of the electrons can be impacted by acceleration them through a potential, supplying the electron with a kinetic energy. For typical TEM studies, the electrons are accelerated through a high voltage potential of 80 keV to 300 keV, giving a wavelength between 4.18 pm and 1.97 pm. With this size of wavelength, it becomes possible to resolve objects and structures at the atomic scale, which is of interest for catalysis. Today, modern state-of-the-art microscopes provide a resolution limit down to 50 pm [7], corresponding to the physical resolution limit for electron probes defined by the Bohr radius ($a_0 = 0.529$ Å) [6], and a single-atom sensitivity [8, 9].

2.1.1 The Transmission Electron Microscope

The TEM microscope can be divided into three main parts; the illumination system, the image formation system, and the projection system. Figure 5 illustrates the physical position of these three parts for the FEI Titan 80-300 ETEM microscope that has been used during
Figure 5: The FEI Titan 80-300 ETEM microscope. The microscope is located at Haldor Topsoe A/S, Denmark, and have been used for all the experiments present in this thesis. The microscope divided into three main parts, the illumination system, the image system and the projection system. Photo adopted from Helveg et al. [10].

this PhD project. The top part of the microscope is the illumination system, which holds the electron source together with the condenser lenses and apertures. The illumination systems generates the electron from the electron source, accelerates the electrons to a given energy, and forms a beam on the specimen. The Titan microscope is equipped with a Schottky field emission gun (FEG), which has the advantage that it generates electrons with a low energy spread. The energy spread is an important factor when it comes to the aspect of high-resolution. To obtain the best possible resolution, all electrons must have identical frequency (i.e. wavelength), which is referred to as temporal coherence. The temporal coherence is a measure for how similar the wave packets are and is depending on the energy spread. Furthermore, the FEG also helps improve the spatial coherence by minimizing the source area from which the electrons are emitted [6]. The aspects of the temporal and spatial coherence is further debated in Section 2.1.3 where the theory behind high-resolution transmission electron microscopy (HRTEM) is addressed.

As the electrons are emitted, they are accelerated in a high voltage potential of typically 80 kV or 300 kV to obtain the desirable wavelength. The electrons are sent down along the optical axis of the microscope where they meet the condenser system. For the Titan
microscope, the condenser system consists of a three condenser lens system with two condenser apertures. The condenser lenses and apertures help controlling the physical size of the electron beam on the specimen and the strength of the beam, i.e. the electron dose rate.

Conventionally, the TEM microscope can be operated in two distinct modes; i) conventional TEM mode, where the specimen is illuminated with a parallel beam or ii) scanning TEM (STEM) mode, where the beam is focused on to and scanned over the specimen. The illumination and projection system for both modes is essentially identical and most standard TEM microscope provides the ability for operation in STEM mode. The work presented in this thesis is conducted in TEM mode and thus, there will not be elaborated further on the STEM operation mode. Hence, for the rest of the thesis, the beam is considered as a parallel illumination on the specimen.

After the illumination system the electrons enter the image formation system where the specimen is located. The image formation system is physically positioned at the middle of the microscope, as illustrated in Figure 5. At this stage, the specimen is inserted in between the upper and lower objective lenses by use of a specimen holder.
When the parallel electron beam penetrates through the specimen, a fraction of the electrons will scatter elastically by the specimen, exciting the specimen in an angle compared to the parallel non-scattered electrons. The lower objective lens, which works as a convex lens, will focus the transmitted electrons toward a plane below the specimen, named the *image plane*. The situation is illustrated by the ray diagram in Figure 6. Electrons that are scattered at the same location in the specimen (the *object plane*) will meet up in the image plane, forming an image of the specimen. On the transition to the image plane, the electrons pass through the *back focal plane*. In the back focal plane, electrons that are scattered by similar angles will meet up, forming a *diffractogram* of the specimen. The diffractogram, or diffraction image, is caused by Bragg diffraction \([6, 11]\) and contains information regarding the crystallinity of the specimen.

The projection system consists of a number of lenses, which job is to magnify the image received from the image formation system to a desirable size. The magnification is performed by spreading the beam toward higher angles. The projection system can either project the image plane to create an image of the specimen, or the back focal plane to form a diffractogram, which is determined by use of the intermediate lens. The magnified image is sent directly to the charged coupled device (CCD) camera, the fluorescent screen for visualization of the specimen, or to the Gatan image filter (GIF) for energy analysis, all located below the projection system.

### 2.1.2 Image Formation

At the point where the transmitted electrons arrive to the CCD camera, the electrons are converted into an image. What the image displays, is the intensity of the electron wave after transmission of the specimen. In the transmission, the electrons interact with the specimen, which results in both amplitude and phase modulation of the electron wave. These modulation will appear as features in the image. For the human eye to register features in an image, the difference in intensity between two adjacent areas has to be significant. This difference in intensity \((I)\) is in practise known as contrast \((C)\) and can mathematically be expressed as

\[
C = \frac{I_2 - I_1}{I_1}
\]

for two adjacent areas \((1 \text{ and } 2)\). The human eye is only able to detect changes in intensity that are larger than 5-10%. Thus, image contrast is often electronically enhance to levels detectable for the human eye.

To understand how the contrast in the TEM image arise, it is necessary to look into the electron-specimen interactions. When the electrons penetrates through the specimen the majority of the electrons
are transmitted without undergoing any scattering events, especially if the specimen is very thin. These electrons are known as the direct beam and maintain their parallel trajectory. In contrast, the rest of the electrons will eventually undergo scattering while travelling through the specimen. The scattering can be distinguished by two scenarios; elastic scattering, where the kinetic energy of the electron is conserved, or inelastic scattering, where the electrons lose kinetic energy to the specimen. Here, the interest lies on the elastically scattered electrons as the image contrast stems from these. However, the inelastically scattered electrons are of supreme importance as well, as they carry essential information about the thickness and element composition of the specimen in terms of their energy loss. It is also the inelastically scattered electrons that are the origin to energy dispersive x-ray spectroscopy, which provide information of the elemental composition of the specimen. The subject of the electron energy-loss (EEL) will be reviewed later in Section 2.4, while the subject of x-ray spectroscopy will be abandoned here.

When elastically scattered, the electrons will experience a change in its direction as it moves through the potential caused by the nucleus in the specimen. The changes in direction of the elastically scattered electrons will eventually vary the intensity profile of the image and hence introduces contrast features in the image. This contrast features are associated to amplitude contrast, which is divided into mass-thickness contrast and diffraction contrast. The mass-thickness contrast is related to the Rutherford scattering and is strongly depending on the atomic number of the specimen. Thus, heavier atoms scatters the electrons more strongly compare to lighter atoms, due to a stronger Coulomb force. As a result, lighter materials will appear more intense than heavier materials in the image. This modulation is entitled the mass contrast \([6]\). If the thickness of the specimen is increased, the chance of electron-nucleus scattering is enhanced. Eventually, more scattering events will result in electrons getting scattered to accumulatively higher angles, where they no longer contribute to the image intensity. Consequently, this leads to an intensity difference between specimen areas of different thickness. This variation in contrast is known as the thickness contrast \([6]\).

The last amplitude contrast mechanism is the diffraction contrast. For crystalline specimens, specific orientation of the crystal lattice will allow for coherent elastic scattering of the electrons as stated by Bragg’s law, resulting in a very distinct angular change of their directions defined by the crystal structure of the specimen. The electrons that undergo Bragg scattering are focussed to a spot in the back focal plane of the objective lens (see Figure 6), where it creates a diffractogram. From such a diffractogram, the structural information of the specimen can be extracted.
Contrast can also arise from differences in the phase of the electron wave and is known as phase contrast. Phase contrast is closely connected to the diffraction contrast of crystalline specimens and is the underlying mechanism for HRTEM, where the atomic structure is imaged in terms of lattice fringes. This phenomenon is an effect of the interference between the coherent elastically scattered electrons and the direct beam. The next section will elaborate on the phase contrast in terms of HRTEM.

2.1.3 High-Resolution Imaging

The high-resolution information in TEM images is a result of the phase changes imposed on the electron wave as it transmits through the specimen. These phase changes affect the phase contrast in the images, which provides the foundation for imaging atomic columns and lattices. To fully interpret the phase contrast in an image, especially at high spatial frequencies, a description of the interaction between the incoming electron wave and the specimen is needed, along with the microscope’s ability to transfer the wave function to the image.

How the incoming electron wave is transmitted through the specimen, depending on the spatial coordinate \((x, y)\), is described by the specimen transfer function \(f(x, y)\), which can be expressed as \(6\):

\[
 f(x, y) = A(x, y) \exp[-i\phi_t(x, y)].
\]

Here, \(A(x, y)\) is the amplitude and \(\phi_t(x, y)\) the phase, where the phase depends on the electrostatic potential that the electron sees when traveling through the specimen. For the application to HRTEM, certain assumptions and simplifications will be made for the model representing the specimen interaction of the electron wave.

First, the incident electrons are assumed to be parallel and monochromatic plane waves. The model is simplified by setting the incident wave amplitude to unity, i.e., \(A(x, y) = 1\). By applying the weak phase object approximation (WPOA) (i.e., the sample is very thin), the electrostatic potential is well described by the projected potential along the beam direction \(V_t(x, y) = \int V(x, y, z) dz\), defining \(z\) as the direction of the electron beam. Moreover, the WPOA also neglects the absorption of electrons in the sample and assumes that \(V_t(x, y) \ll 1\) \([6]\). With this, the electron exit wave after the specimen \(\phi_{obj}(r)\), denoted by the in-plane position vector \(r = (x, y)\), becomes \([6]\)

\[
 \psi_{obj}(r) = \exp[-i\sigma V_p(x, y)] \approx 1 - i\sigma V_p(x, y),
\]

where \(\sigma\) is an interaction constant.

After escaping the specimen, the electron exit wave propagates through the microscope imaging system (lenses, apertures, and possible image corrector) towards the acquisition device. Here, the electron wave becomes affected by the microscope imaging system and,
thus, the final image recorded at the acquisition device will become a convolution between the electron exit wave and the contrast transfer function (CTF) of the imaging system. The image intensity is the absolute square of the modulated electron wave and, by neglecting higher order terms of $\sigma$, it becomes [6]

$$I(r) \approx 1 + 2\sigma V_p(x, y) \otimes \mathcal{F}^{-1}\{\text{CTF}(u)\} \quad (9)$$

Here $\mathcal{F}^{-1}$ is an inverse Fourier transformation and CTF$(u)$ is the contrast transfer function of the microscope presented in the spatial frequency domain $u$, or in Fourier space, where $u \propto 1/r$. Equation 9 gives a description of the final images, where the first term denotes the electron-specimen interaction and the last term describes the imaging process of the electron.

The CTF is especially crucial for the image interpretation, as it holds the key to how the information is delivered to the image. The CTF is defined as [6]

$$\text{CTF}(u) = A(u)E(u)2\sin\chi(u), \quad (10)$$

where $A(u)$ is the aperture function, and essentially a step function, which cuts off all spatial frequencies higher than the value permitted by the possible objective aperture size. $E(u)$ is the envelope function, which describes the damping at higher spatial frequencies due to spatial and temporal incoherence. The damping is determined by the properties of the objective lens and the electron source. Lastly, $\chi(u)$ is the aberration function and describes the effect of the objective lens aberration on the transmitted wave. Thus, the aberration function is a product of the spherical aberration of the objective lens (spherical aberration ($C_s$)), the acceleration voltage (expressed in terms of the wavelength, $\lambda$), the defocus value ($\Delta f$) and the spatial frequency ($u$), and can be expressed as [6]

$$\chi(u) = \pi\Delta f\lambda u^2 + \frac{1}{2}\pi C_s\lambda^3 u^4 \quad (11)$$

Here, only the defocus and spherical aberration terms is included as the remaining and higher order terms (coma, astigmatism, etc.) normally is corrected before the start of an experiment.

To elaborate on the microscope’s ability to transfer the contrast of the transmitted wave function, the aperture function $A(u)$ and the envelope function $E(u)$ will be ignored for a start, leaving only the aberration function to consider. In principle, $\sin(\chi(u))$ describes how the phase contrast is represented in the recorded image. At negative values, the CTF returns a negative phase contrast that will image the atomic columns as dark on a bright background compared to vacuum. Similarly, a positive value of CTF will return a positive phase contrast, giving bright atoms on a dark background. Thus, it becomes import to know what phase contrast regime a given spatial frequency belongs to when an image is interpreted.
Figure 7: Aberration function for a non $C_s$-corrected TITAN microscope. Here shown at defoci 0 nm and −54 nm, where the latter is the extended Scherzer defocus for the presented parameters. The $\sin(\chi)$ is calculated by applying of Equation 11, using a $C_s = 1$ mm and a primary electron energy of 300 keV.

Figure 7 displays a one-dimensional plot of $\sin(\chi(u))$ for a microscope with a spherical aberration constant of $C_s = 1$ mm and operating at a primary electron energy of 300 keV. Here, $\sin(\chi(u))$ is plotted for two different foci; at 0 nm defocus (focus) and at −53 nm defocus (underfocus). From Figure 7, it is seen that $\sin(\chi(u))$ starts at zero, which means that no phase contrast is transferred. However, at low spatial frequencies ($u$) correspond to vast distances in real space this is not a problem. For low spatial frequencies, the defocus term ($\pi \Delta f \lambda u^2$) in Equation 11 dominates the value of the $\sin(\chi(u))$ function. Therefore, operating at underfocus (i.e. $\Delta f < 0$) the CTF will return a negative phase contrast response. Increasing the spatial frequency, the two terms in Equation 11 will start equal out each other and the first cross-over will appear at $u_1$, i.e. meaning that no phase contrast is transferred for this spatial frequency ($u_1$). This point is known as the point resolution. After the point resolution, the CTF starts to oscillate between a positive and negative phase contrast response. Eventually, this means that spatial frequencies above the point resolution can not directly be interpreted due to the periodic change in sign.

For zero or positive defocus, the CTF will transfer a positive phase contrast up until the first cross-over (the point resolution), which will occur at lower spatial frequencies than for negative defocusing values. Therefore, the microscope is normally operated with a negative defocus value (underfocus) to obtain the largest possible pass-band
of spatial frequencies where the frequencies are transferred with the same sign.

The best optimized pass-band can be achieved by balancing a negative defocus against the spherical aberration of the microscope. This leads to the defocus value known as the extended Scherzer defocus, given as

$$\Delta f_{Sch} = -\sqrt{\frac{4}{3} C_s \lambda}$$  \hspace{1cm} (12)

At this defocus, the point resolution is moved to the highest possible $u$-value for what the microscope can perform, returning a nearly constant contrast up until a resolution of

$$r_{Sch} = 0.66C_s^{\frac{1}{2}}\lambda^{\frac{3}{4}}$$  \hspace{1cm} (13)

Thus, this focus value is the preferred point of operation. For the microscope parameter used in Figure 7, the extended Scherzer focus is obtained at $\Delta f_{Sch} = -54$ nm and is displayed by the blue curve.

In principle, the $\chi(u)$ function can be extended as far as wanted, but in reality, the function is damped by the envelope function $E(u)$. Therefore, the envelope function is now reintroduced into the expression of the CTF such that its influence on the attenuation can be elucidated. In Figure 8 the CTF is displayed, consisting of the $\sin(\chi(u))$ term (displayed in Figure 7) and the envelope function $E(u)$. The
CTF is calculated by help from the ctfExplorer software [12, 13], using a spherical aberration of \( C_s = 1 \text{ mm} \), a chromatic aberration of \( C_c = 1.4 \text{ mm} \), a primary electron energy of 300 keV, an energy spread of 0.6 eV, a high tension ripple of 1 ppm and a convergence angle of 0.3 mrad. In the figure, the CTF is plotted at extended Scherzer focus \( \Delta f_{\text{Sch}} = -54 \text{ nm} \) (blue curve), together with the spatial envelope (red curve), the temporal envelope (green curve) and the combined envelope (orange curve).

From Figure 8, it is seen that the introduction of the envelope function does not influence on the position of the point resolution, which maintains stable at 0.19 nm (or \( u = 5.26 \text{ nm}^{-1} \)). However, the envelope function does attenuate the contrast dramatically at higher spatial frequencies, leaving the CTF at zero value for frequencies higher than approximately \( u = 10 \text{ nm}^{-1} \) (or distance lower than 0.1 nm). In principle, information can be gathered as long the absolute value of the CTF exceed a value of \( 1/\exp(2) \) [14, 15]. The point where the CTF is suppressed below this value is termed the information limit, and is illustrated in Figure 8 at spatial frequency of \( u = 7.7 \text{ nm}^{-1} \) (or 0.13 nm). The spatial coherency is a major factor that affects the information limit, and is defined by the convergence of the incoming electron wave. Also the temporal coherency envelope attributed to the damping of the contrast, but to a lesser extent. Here, the temporal envelope is defined by the chromatic aberrations, the energy spread as well as the instability of the high tension. To improve the information limit of the microscope, the spatial coherency has to be enhanced. This can be achieved by correcting for the \( C_s \) of the objective lens.

The microscope used in this thesis, the FEI Titan 80-300 ETEM, is equipped with a CEOS image corrector, which allows for correction of the spherical aberration of the objective lens. Reducing the spherical aberration to a typical operation value of \( C_s = -10 \mu \text{ m} \) will improve the CTF significantly (i.e. both the point resolution and the information limit shift towards higher spatial frequencies, and the extended Scherzer defocus value moves closer to zero). Figure 9 displays the CTF after correcting the spherical aberration down to a value of \( C_s = -10 \mu \text{ m} \). All remaining parameters are kept the same as in Figure 8. As a result of the \( C_s \)-correction, the resolution limit is now improved to approximately 0.08 nm (or \( u = 11.8 \text{ nm}^{-1} \)) while operating at the extended Scherzer focus (\( \Delta f = -5 \text{ nm} \)).

Another aspect of the \( C_s \)-correction is that the extended Scherzer defocus has moved towards lower values. This has shifted the point resolution to a spatial frequency beyond the resolution limit. Also, it lead to a narrower contrast response, especially for low spatial frequencies. This means that larger features, such as particle outlines may become very weak in images obtained at condition favourable for lattice fringes. Therefore, it can sometimes be beneficial to oper-
Figure 9: Contrast transfer function for a C₅-corrected Titan microscope. Here, depicted with defoci of −4 nm and −8 nm. The CTF is calculated using CTFExplorer [12, 13], with Cₛ = 1 µm, Cₐ = 1.4 mm, HT of 300 keV, energy spread of 0.6 eV, HT ripple of 1 ppm and convergence angle of 0.3 mrad. Also, the spatial envelope (red), the temporal envelope (green) and the combined envelope (orange) is included.

ated at lower defocus value to increase the contrast response as illustrate in Figure 9 for Δf = −8 nm, however, it comes at the expense of a lower point resolution. Luckily, the Cₛ-correction also helps to eliminated the delocalization of the phase contrast, meaning that the lattice fringes resolved in a nanoparticle will remain within the outline of the particle and not extend over the edge.

In conclusion, the Cₛ-corrected Titan microscope distinguishes itself by having a resolution limit of 0.08 nm and being without any contrast reversal. These facts, together with its ability to eliminate the delocalization, makes it ideal for performing HRTEM imaging of catalysts. In the following, we will go into the consideration of other aspects needed for HRTEM.

2.1.4 Electron Imaging in Practice

The description given above builds on the scenario that the image signal is not a limiting factor for image formation. However, this is often not the case, since specimen thickness, specimen drift, specimen sensitivity, detector efficiency, et cetera limit the attainable image signal. From the report of Rose (1948) [16], it was determined that the signal-to-noise ratio (SNR) in an image has to surpass a ratio of 5 before the human eye was able to detect the image features. The SNR of an
image is conventionally defined as the ratio between the mean pixel intensity $n_{\text{mean}}$ and the standard deviation of the pixel intensities $\sigma_n$:

$$\text{SNR} = \frac{n_{\text{mean}}}{\sigma_n}$$

(14)

Following the statement from Rose, the attainable resolution ($d_s$) can be expressed as $[17, 18]$

$$d_s = \sqrt{d_i^2 + \frac{\text{SNR}^2}{C^2D}}$$

(15)

The equation relates the attainable resolution ($d_s$) to the native resolution limit of the microscope ($d_i$), the image contrast ($C$) described by Equation 6, and the accumulated electron dose ($D$), which denotes the number of incident electrons delivered to the specimen per unit area and has the unit [e$^-$/Å$^2$]. Furthermore comes that the Nyquist-Shannon sampling theorem [19] must be satisfied to ensure the validity of the image resolution. The theorem in practice says that to acknowledge that a signal is sincere, the sampling rate used to decode the signal has to be less than half the size of the signal. That means that the attainable and validated image resolution becomes $d_{\text{res}} = 2d_s$. Consequently, it means that the attainable resolution in practice becomes a question of obtaining a significant electron dose in the TEM image, cf. Equation 15.

In practice, the accumulated electron dose ($D$) is set by the electron dose rate ($r$) and the exposure time ($t$). For dynamic experiments, the exposure time becomes limited, $t_{\text{cutoff}}$, by the characteristic timescale of the dynamic process, the drift of the specimen and the stability of the electron optics. To attain an accumulated electron dose necessary to resolve atomic-scale features, the electron dose rate must match the finite exposure time. If the electron dose rate is set to low $r_{\text{min}}$, the accumulated electron dose will not surpass the necessary level for obtaining the atomic resolution, set by the Rose criterion. However, the electron dose rate cannot be enhanced blindly, as too high electron dose rates often lead to beam induced effects as addressed by Kisielowski [20] and, which also will be demonstrated later on in the thesis. This leaves a narrow parameter window in which the TEM experiments can be conducted.

The present discussion is sketched in Figure 10 and displays the relationship between the accumulated electron dose, the electron dose rate and exposure time. Figure 10 illustrates how the operational parameter space gets limited by a threshold value ($D_{\text{Rose}}$) for the accumulated electron dose needed to ensure the desired resolution and finite exposure time ($t_{\text{cutoff}}$). At the same time, the electron dose rate must be significantly low ($r \leq r_{\text{max}}$) such as to oppress invasive illumination conditions. This leaves an operational parameter space
Figure 10: Schematics of the operational parameter windows for HRTEM under non-invasive illumination. The parameter window is determined by the need of electron dose, the limit of exposure time and the limit of electron dose rate. The figure is adopted from Helveg et al. [10] and modified.

(indicated by blue in Figure 10) restricted by the accumulated electron dose threshold ($D_{\text{Rose}}$), the finite time ($t_{\text{cutoff}}$) and the electron dose rate ($r_{\text{min}} \leq r \leq r_{\text{max}}$). It should be stressed that the parameter space heavily depends on the catalyst and the environmental conditions. It is most difficult to predict the parameter space prior to an experiment and it should, therefore, be experimental investigates to accommodate and oppress such beam effects.

### 2.2 in situ TEM

TEM is by origin a vacuum technique, meaning that the microscope column, in which the electrons travel, has to be kept under vacuum conditions upon operation. This is due to the constraint for operating the Schottky FEG, which requires a background pressure below $1 \times 10^{-8}$ mbar [6], but also to limiting collision between the electron and the gas molecules, which eventually will reduce the signal and hence the resolution, according to the discussion in Section 2.1.4.

Within the field of heterogeneous catalysis, the aspect of vacuum techniques tends to be problematic as the investigation is limited to pre mortem and post mortem studies. That excludes the possibility to study dynamic reactions and equilibrium reactions, where the equilibrium structure depends on the combination of gas and temperature. Therefore, it is desirable to circumvent the nature of the microscope, so that it allows for in situ experiments without the deterioration of the signal. Here, in situ is Latin for “on site” or “in position”, and entails that the reaction is observed while it occurs. This often means
that the catalyst is observed while exposed to one or more reactive gases and elevated temperature.

The principle of such an in situ environmental cell (e-cell) is illustrated in Figure 11. The idea of the e-cell is to localize the gas around the specimen while keeping the crucial part of the microscope, such as the FEG, under its normal vacuum condition. Furthermore, it is desirable to implement the possibility for heating the specimen and thereby approach more realistic reaction conditions for the catalyst. Finally, the e-cell should be designed in such a way that the electron beam can probe the catalyst.

An e-cell, where both the gas pressure and the temperature are controllable, can be employed to the TEM microscope by the principle of differential pumping [21, 22] or by a closed window cell [21, 23]. In the following, the concept of these two methods, starting with the differentially pumped microscope, will be reviewed.

2.2.1 The Differentially Pumped System

The differential pumped system of the FEI Titan 80-300 ETEM microscope is base on the design of Boyes and Gai (1997) [22], where the concept is to differentially evacuate individual stages of the microscope column, which are separated by pressure-limiting apertures. However, in addition to the design suggested of Boyes and Gai [22], an extra pumping stage has been introduced to ensure a better protection of the FEG. Figure 12 illustrates the individual vacuum stages of the microscope column.
Figure 12: The differentially pumped vacuum system of the FEI Titan 80-300 ETEM. The sketch illustrate the individual vacuum stages of the microscope column, separated by the pressure-limited apertures. The first and second stage are pumped by turbo-molecular pumps (TMPs). A third stage located at the C1 is pumped by an ion getter pump (IGP). The reactive gas is introduced locally around the specimen, from where it leaks out of the pressure-limited apertures and are pumped away. The figure is adopted from Hansen, Helveg, and Datye [25].

The differentially pumped system establishes an e-cell in the microscope column, defined as the volume between the objective lens pole pieces (at 5.4 mm) [24], which also hosts the specimen. Here, the gaseous environment is introduced and confined around the specimen by restricting the gas flow above and below the specimen. From the e-cell, the gas diffuses out through the apertures and into the first vacuum stage, which is pumped by a turbo-molecular pump (TMP), displayed as TMP1 in Figure 12. The TMP’s ability to remove the flowing gas is so efficient that the pressure is reduced by a factor of $10^3$ after the first differential step. Above the first vacuum stage, two additional vacuum steps are present. Here, the second vacuum stage is pumped by an additional TMP (TMP2), where the third vacuum stage is pumped by an ion getter pump (IGP). Each of the stages reduce the pressure further by a factor of $10^3$, resulting in a pressure of $10^{-9}$ mbar at the FEG. Consequently, the required pressure for emission in the electron source is obtained through the used of differential pumping [6].

The differentially pumped system offers an operational pressure regime from vacuum to $20$ mbar within the e-cell depending on the
type of gas [24]. As the gas is introduced to the e-cell, the atomic density increases along the electron beam direction in the e-cell as well as in the microscope column. That eventually results in an enlargement of electron scattering by the gas molecules. The gas introduced in the e-cell can be thought of as an additional solid thickness added to the specimen. Using the atomic density of graphite (1.14 × 10^{29} \text{ atoms/m}^3) as the reference, the gas density can be related to an equivalent solid thickness. If so, a 1 mbar diatomic gas at room temperature (RT) (298 K), present in the e-cell, will be equivalent to a solid thickness of 3.2 nm, where a pressure of 20 mbar will be equivalent to a thickness of 63 nm. At these high pressures, the equivalent thickness approach a thickness larger than the specimen itself. Even though that it is possible to achieve high-resolution at these pressure regime [24, 26], the image intensity and the resolution will in the end be limited by the gas phase. This fact, together with a finite pumping capacity of the TMPs, will eventually restrict the differentially pumped microscope to a pressure regime within the mbar range.

The differentially pumped TEM microscope offers great possibilities, which have led to many exciting discoveries [27–31] since its development back in 1997 [22]. However, for some types of experiments a higher pressure is needed than the 20 mbar offered by the differentially pumped microscope. That is due to the reaction kinetics, which displays a power law dependency of the partial pressure, but also the chemical potential, which demonstrates a logarithmic dependency of the pressure [5]. In that case, a closed window cell is needed.

### 2.2.2 The Nanoreactor System

To attain an ambient pressure within the TEM microscope, the height of the gas phase must be reduced a 1000-fold to compensate for the increase of the pressure. If not, the increased number of gas molecules present along the path of the electrons will eventually degrade the image signal, and thereby the resolution, due to the increase of electron scattering by the gas molecules. Limiting the gas to a volume height of only a few µm is unachievable by use of differential pumping, which therefore requires rethinking of the working concept. Moreover, the restricting of the gas must not compromise the inclusion of the specimen itself nor the demand for elevation of the temperature, which makes the process challenging.

One option is to encase the gas and specimen by thin membranes as presented by Butler and Hale [21]. The very first attempts of such closed window cells was made back in 1944 by Abrams and McBain [32] using polymeric window materials. Today, the advantages of silicon technology and clean room fabrication have taken over, allowing
delicate fabrication on the nano-scale. That has resulted in numerous closed window designs made from silicon wafers, and is colloquially referred to as NRs. [23, 33–37]

The development of the NRs of today was carried out by a collaboration between TU Delft, the FEI company (today a part of Thermo Fisher Scientific) and Haldor Topsoe A/S and started in 2003. The project was later continued within the NIMIC consortium1 [38]. In 2008, the first report on the NRs was published [23]. Herein, Creemer et al. demonstrated a multidimensional micro-electro-mechanical system (MEMS) NR, containing an uni-direction flow micro-channel, in which the gas was constrained to a gas height of 4 µm [23]. The NR was fabricated from silicon wafers by assemble two facing dies using wafer bonding. At the middle of each of the two dies, a 1 mm × 1 mm hole was etched, over which a 1.2 µm silicon nitride membrane was mounted. In the center of the membranes, an array of 10 nm thick electron-transparent windows were created, which allows for examination of the specimen loaded into the NR. At the top membrane, in-between the electron-transparent windows, a spiral Pt element was positioned and used for temperature sensing and control. By applying a power trough the Pt element, the center of the flow channel - known as the reactor zone - could be resistively heated from RT to 500 °C. With this reactor, the group demonstrated an atomic resolution of 0.18 nm for a Cu nano-crystal at 500 °C while exposed to 1.2 bar of H₂ [23].

It later turned out that the presented reactor design suffers for bulging of the membranes as the pressure rose with respect to vacuum [33, 39]. The bulging resulted in a considerable variation of the gas height, which is untenable while studying catalytic activity. Furthermore, the assembly of the two dies turned out challenging, as most of the wafer bonding techniques cannot be applied to the NRs due to contamination issues [40]. Eventually, it lead to a new design of the NR, where the NR was entirely integrated into a single die, resulting in a hermetically sealed reactor. Moreover, the new design involved stabilizing pillars within the gas channel, preventing the membranes from bulging. This new design is depicted in Figure 13 and gives basis to the reactor designs used in this thesis.

2.2.3 Comparison of Nanoreactor Designs

Today, numerous reactor designs are available [23, 33–37], all try to minimize the height of the gas channel as well as the thickness of the windows as much as possible. However, there is a limitation for how narrow the window as well as the channel can be, in terms

---

1 The NIMIC consortium (Nano-IMaging under Industrial Conditions) is aimed at making a wide variety of physical, chemical and biological processes visible that take place on the scale of atoms and molecules.
of the integrity of the windows and the loading process of the reactor. Among the commercial ones, the DENS solutions reactor (climate) [34] and Protochip reactor (Atmosphere) [35] is probably the most commonly knowns. However, in this thesis, two alternative reactor designs are employed, namely the Dimes NR and the Thermo Fisher NR. These two designs distinguish themselves from the above mentioned reactor designs by:

- Being hermetically closed
- Employing stabilizing pillars
- Restricting the height of the gas to below 5 µm
- Having only 15 nm thin electron-transparent windows
- Not allowing the gas to bypass the heated reactor zone

All are important aspects for attaining constant and reliable conditions needed for studying catalysts. A comparison between the two reactors and the commercial available reactor design, here represented by the DENS solution climate NR, is presented in Table 1.

The main difference between the NRs used in this thesis and the commercialized NRs is that the Dimes and the Thermo Fisher NRs are hermetically sealed, whereas the commercialized reactors are sealed by use of a O-ring. That, of course, makes the loading process easier for the commercialized NRs, as the reactor can be disassembled, but it comes with the drawback of a higher and unstabilized (no pillars) gas channel. This will, together with the thicker windows, results in an increase of electron scattering and hence, a degradation of the image signal. However, most critical is the gas bypass around the heating zone. Both the Dimes and the Thermo Fisher reactor does not allow...
**Table 1: Specification of the nanoreactors utilized in this thesis.** The table compares the specification of the Dimes and the Thermo Fisher NRs. The DENS solutions climate NR is included as reference to the commercialized reactors available for sale. Data is obtain from [33, 34]

<table>
<thead>
<tr>
<th></th>
<th>Commercialized</th>
<th>Non-Commercialized</th>
<th>Non-Commercialized</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DENS SOLUTION</td>
<td>Dimes</td>
<td>Thermo Fisher</td>
</tr>
<tr>
<td>Gas channel height</td>
<td>10 µm</td>
<td>4.5 µm</td>
<td>2 µm or 5 µm</td>
</tr>
<tr>
<td>Gas channel width</td>
<td>–</td>
<td>280 µm</td>
<td>280 µm</td>
</tr>
<tr>
<td>Gas channel length</td>
<td>–</td>
<td>5.4 mm</td>
<td>5.4 mm</td>
</tr>
<tr>
<td>Number of windows</td>
<td>10</td>
<td>41</td>
<td>11</td>
</tr>
<tr>
<td>Window diameter</td>
<td>6 µm</td>
<td>6 µm</td>
<td>4 µm</td>
</tr>
<tr>
<td>Lower window thickness</td>
<td>30 nm</td>
<td>15 nm</td>
<td>15 nm</td>
</tr>
<tr>
<td>Upper window thickness</td>
<td>30 nm or 50 nm</td>
<td>15 nm</td>
<td>15 nm</td>
</tr>
<tr>
<td>Stabilizing pillars</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Pillars size</td>
<td>N/A</td>
<td>10 µm</td>
<td>30 µm</td>
</tr>
<tr>
<td>Pillars distance</td>
<td>N/A</td>
<td>20 µm</td>
<td>35 µm</td>
</tr>
<tr>
<td>Heater area</td>
<td>9.0 × 10³ µm</td>
<td>6.7 × 10⁴ µm</td>
<td>3.5 × 10⁴ µm</td>
</tr>
<tr>
<td>Temperature range</td>
<td>RT to 1000 °C</td>
<td>RT to 660 °C</td>
<td>RT to 670 °C</td>
</tr>
<tr>
<td>Gas bypass</td>
<td>–</td>
<td>0 %</td>
<td>0 %</td>
</tr>
<tr>
<td>Sealing</td>
<td>O-ring</td>
<td>single die (hermetic sealed)</td>
<td>Silicon fusion bonding (hermetic sealed)</td>
</tr>
</tbody>
</table>

The majority of the work reported in this thesis has been obtained by use of Dimes NRs, which is depicted in Figure 14. A full description of the reactor design and the fabrication is given in [33]. The Dimes NRs stands out from the rest by being integrated entirely into a single die by use of micromachining. This fact, together with the implementation of stabilizing pillars, has increases the strength and rigidity of the reactor, allowing a pressure of 14 bar before breaking.

For the Thermo Fisher NRs, displayed in Figure 15, the reactors are assembled from two dies by use of Silicon fusion bonding [40]. As an extra feature, the Thermo Fisher NRs come with a vacuum inside the flow channel, enclosed by thin membranes, which are punctured during the loading procedure. Besides ensuring a clean channel surface during transport, the vacuum also refines the loading procedure as the vacuum can be facilitated to drag a slurry or precursor solution into the reactor.

Both NRs are resistively heated by four electrodes connected to the heater element, which allows for simultaneous heating and temperature sensing. By monitoring the measured resistance in the heater
with a closed control loop, the temperature remains precise upon changing without any major under- or overshooting \[41\]. Herby, the temperature can be elevated reversibly from RT to around 660 °C. Where the Dimes reactor uses a Pt thin-film hexagon, the Thermo Fischer reactor uses a Mo thin-film shaped as a meander with a circular plate in the center, as illustrated in Figure 15. The circular plate acts as a heat spreader, providing very uniform temperatures across the plate, where the electron transparent windows are positioned \[41\].

The reactor zone of the NRs are defined by the area extended by the heater element. Because the reactor zones only account for around 5% of the total gas channel length, the reactor zone is regarded to be isobar. Due to a symmetric geometry of the reactor, the pressure present in the reactor zone is half the difference between the inlet and outlet pressure. That means if the NR is operated in full flow mode, that an inlet pressure of 2 bar and vacuum at the outlet (typically in the order of \(10^{-1}\) mbar) will result in a pressure of 1 bar in the reactor zone \[33, 42\].

In the consideration of the enlargement of electron scattering introduced by the NR with a channel heigh of 5 µm, the gas phase is now reduced to an equivalent solid thickness of 1.9 nm for a 1 bar diatomic gas at RT. That is a reduction of 40% compared to the differential pumped microscope operating at 1 mbar. In addition to the differential pumped microscope, comes now the two NR windows, each of a thickness of 15 nm. That gives a final solid thickness of
Figure 15: Top view of the Thermo Fisher nanoreactor and its reactor zone. In the middle, the reactor is thinned down to a thickness of 1.5 µm, creating an 1 mm × 1 mm opening that exposes the reactor zone located at the center of the gas channel. In the reactor zone, a meander-shaped heating element is placed, in which, 11 electron transparent SiN\textsubscript{x} windows are positioned in a dime-like pattern. The heater is connected via four electrodes located at the right side of the reactor, which allows for simultaneous heating and temperature sensing.

32 nm that the electrons have to penetrate in addition to the specimen itself. That, however, is still a reduction of 50 % compared to 20 mbar of gas in the differential pumped microscope.

### 2.2.4 Loading of the Nanoreactors

For the NR designs employed in this thesis, the Dimes and Thermo Fisher NRs, the only access to the gas channel, and hence the reactor zone, is through the inlet and outlet connections at the backside of the reactor (see Figure 13 and Figure 14). To load the NR, the catalyst materials have to enter through one of those connections. The catalyst material can be prepared in two ways;

- the catalyst is synthesized outside the NR and afterwards introduced in form of a slurry
- the catalyst is synthesized inside the NR, introduced as a salt solution

The NR is loaded by drop casting the slurry or the salt solution on the inlet connection of the reactor, from where the capillary forces will drag the slurry or the solution into the micro-channel and toward the reactor zone. After the liquid phase has evaporated, the reactor temperature is shortly elevated past 100 °C to remove all possible water and, in case of the salt solution, to fully decompose the salt. The reactor is afterwards mounted in the microscope, where calcination and reduction takes place, if required.
The Nanoreactor Holder

The NR is inserted into the TEM microscope by the use of a custom made holder from Thermo Fisher Scientific. The tip of the holder is shown in Figure 16 together with a Thermo Fisher NR. Here, the NR is mounted in the carving in the holder top and secured by a lid (not displayed here). In the middle of the carving a hole is made, allowing the electrons to pass through while examining the NR.

Four spring electrodes, located at the back of the carving, provides electrical connection to the reactor. Through this connection, the temperature of the reactor zone can be monitored and elevated by a software using proportional-integral algorithms to control the heating. The system can either be run in constant power mode or constant temperature mode, where only the latter has been used in this report.

In the bottom of the carving, an inlet and outlet connection are placed, connecting the reactor to the gas handling system via two ceramic tubes located inside the holder shaft. Typically, the gas is fed into the reactor by the inlet line, while the outlet line is connected to a MS for analysis of the exit gas and is pumped by a TMP. The connection is sealed by two o-rings, as seen on Figure 16.

2.3 Mass Spectrometry

Since the majority of the products created under the catalytic reaction are present within the gas phase, they cannot be observed directly by the microscope in real time. By utilizing mass spectrometry, the gaseous compounds can be analyzed by means of a mass-to-charge
ratio close to real time. Several types of MSs exist today, where the QMSs and time-of-flight MS are the most common. A first description of such MSs was given in 1953 by Wolfgang and Steinwedel [43].

At the FEI Titan 80-300 ETEM microscope, two quadrupole mass spectrometers (QMSs) is employed for measuring the exit gas of the microscope. One dedicated for the in-column e-cell and another dedicated for the NR, both being a Pfeiffer PrismaPlus® QMS 220 M1. In the following, a description of how the QMS works is given.

2.3.1 Quadrupole Mass Spectrometer (QMS)

In general, a MS consists of three main parts; i) an ion source for ionizing the gas, ii) a mass filter for filtering the molecules by means of the mass-to-charge ratio, and iii) a detector for detecting the filtered molecules. These are all illustrated by Figure 17.

The exit gas from the in-column e-cell or NR are guided into the MS by use of pumping, where the gas molecules first enter the ionizer. In the ionizer, electrons are emitted from a filament and accelerated between an anode and cathode. As the neutral gas molecules enter the formation space between the anode and cathode, the molecules will collide with the electrons, forming single or multiple positive ions. These positive ions are then focused into the mass filter by a pair of ion lenses.

In the mass filter, the positive ions are filtered by means of their masses using a quadrupole mass filter. The quadrupole mass filter consists of four parallel, cylindrical electrodes mounted in a square formation as illustrated in Figure 17. The pairs of opposite rods are held at the same potential, composed by a DC voltage \(U\) and a radiofrequency voltage \(V\) with the frequency of \(\omega\). This creates a quadrupole electrical field of a total potential given by

\[
\Phi_0 = U \cdot V \cos(\omega t),
\]

The electrical field will force the ions into a helical motion. By tuning the frequency, the DC and the AC potential, a stable trajectory for the overall ion motion can occur, causing ions of a certain mass-to-charge ratio to pass through the quadrupole.

The filtered ions are electrically detected by a Faraday collector or a secondary electron multiplier (SEM). The Faraday collector is basically a Faraday cup that captures the ions, which will give up their electrical charge. The current is converted into a voltage by use of an electrometer amplifier and sent to the software. With this detection method, the MS can operate up to a maximum pressure level of \(10^{-4}\) mbar to \(10^{-3}\) mbar and with a detection limit of a minimal partial pressure in the order of \(p_{\text{min}} = 10^{-10}\) mbar [44].

If lower detection limits or a higher sampling speed are required, a SEM is used. The multiplier is constructed by a number of dynodes
2.4 Electron Energy-Loss Spectroscopy

When the electron beam transmits the specimen, a fraction of the electrons will be scattered inelastically as described in Section 2.1.2. In these inelastically scattering events, energies are transferred from the electrons to the specimen. Electron energy-loss spectroscopy (EELS) revolves around the information stored in the distribution of the energy lost in the interaction. The EEL is represented in a histogram, known as an EEL spectrum, which displays the fraction of electrons that has gone through an energy-loss of a discreet energy. From analysis of the different features of the EEL spectrum, information can be extracted such as the specimen thickness, the atomic composition of the specimen, the bonding states, etcetera.

In the following, it will be demonstrated how such an EEL spectrum is constructed. To do so, a standard boron nitride (BN) specimen is employed as an example, since this specimen type often is used for calibration of EEL spectra due to its very sharp features. However, first it will be explained how an EEL spectrum is obtained by use of a post-column Gatan image filter (GIF) system.
Figure 18: Schematic of the post-column Gatan Image Filter. The sketch illustrates the principle behind and the elements of the GIF. From the microscope column, the electrons enter the GIF through an entrance aperture, after which they are focused into the drift-tube. Here, the electrons are separated by a magnetic prism according to their energies. The electrons finally pass through the projector system of the GIF towards the CCD camera, where an image or a spectrum are acquired.

2.4.1 Gatan Image Filter (GIF)

The FEI Titan 80-300 ETEM used is operated with a post-column GIF of the model 863 GIF Tridiem®. It is Gatan’s third generation post-column energy filter, which provide a third-order spectrometer aberration correction and comes with a 2K × 2K UltraScan 1000 camera.

The GIF consists of several parts as illustrated in Figure 18. For the electrons travelling along the microscope column towards the GIF system, the electrons first have to enter through the entrance aperture. The entrance aperture defines what portion of the beam that will contribute to the image or spectrum. The GIF Tridiem® system operates with three different aperture sizes (5 mm, 2 mm and 1 mm) plus a mask aperture, where the latter is exclusively used for tuning of the GIF. Next after the entrance apertures comes an optical assembly of pre-prism focusing and alignment lenses, which is used to align the beam and finely correct second-order and third-order aberration of the GIF prism.

The heart of the GIF is a 90° magnetic prism, which separates electrons with different energies. The prism encases the drift tube and generates a magnetic field that will bend the electrons through 90° as the electrons travels down through the drift tube. Core-loss electrons, which have undergone energy loss, will be bend more strongly than
zero-loss electrons, which have not lost any energy and therefore are more energetic. This leads to a vertical separation of the electrons compared to their energies, with the zero-loss electrons located at the bottom and the least energetic electrons at the top.

After the GIF prism, an energy-selecting slit is located at the image plane of the filter system that can be used to single out a specific range of the electron energies. This is particularly used during energy filter TEM, which is beyond the scope of this thesis. Then, the selected electrons travel through the "projector system" of the GIF, which is an assembly of quadrople-sextupole lenses. Like for the in-column TEM projector system, the GIF projector system can run in either image mode or spectroscopy mode. When operated in spectroscopy mode, an energy-dispersed spectrum is formed at the GIF detector plane, while operated in image mode, an image will emerge. The detector is a Gatan Model 894 UltraScan 1000 camera, which use a 2048 × 2048 pixel astronomygrade CCD chip with a pixel size of 14 µm by 14 µm. For a more detailed review of the GIF system, see [6, 45].

2.4.2 The Electron Energy-Loss Spectrum

In the following, the EEL spectrum features will be covered using a BN specimen as the showcase. The BN specimen is special due to its very sharp features and therefore is often used as an external calibration specimen. Figure 19 displays a typical EEL spectrum for a 300 keV electron beam after interaction with a BN specimen. The EEL spectrum is divided into a low-loss (LL) and a core-loss (CL) region, separated by EEL below and above approximately 50 eV [6, 45]. In Figure 19 the LL is illustrated by the blue spectrum and the CL by the red spectrum, where the CL has been scaled compare to the LL. Here, the LL spectrum has been recorded with the microscope’s projector system operating in image mode. In contrast, the CL spectrum presented in Figure 19 is recorded while operated in diffraction mode, which is lucrative for obtaining better SNR and spatial resolution [6].

The LL region represents collective excitations of electrons in the outermost atomic orbitals, also known as valence electrons. Therefore, studies of the LL region is sometimes refer to as valence electron energy-loss spectroscopy (VEELS). The domination feature in the LL region is the plasmon peak located in the range of 3 eV to 40 eV [45, 46], which arises from collective resonant oscillation of the valence electrons. The position of the plasmon peak is governed by the density of the valence electron where as its width is determined by the rate of decay of the resonant mode. Changes in the valence electron density will therefore be detectable as a shift in the plasmon energy, allowing a mean of chemical phases to be identified. Furthermore, properties such as electrical and thermal conductivity are functions of the local valence electron densities. Hence, a free-electron metal will demon-
Figure 19: Electron energy-loss spectrum of a BN calibration specimen. Here, the blue curve represents the low-loss spectrum, including the zero loss and the plasmon peak. The red curve represents the core-loss spectrum, displaying the B-K edge at 188 eV and the N-K edge at 401.6 eV. The core-loss spectrum is scaled compared to the low-loss spectrum.

strate a sharp plasmon peak, while insulators or semiconductors will show a considerably broader plasmon peak [46].

The LL region also holds the zero loss peak (ZLP), which consist of electrons that are transmitted without suffering measurable energy loss, including all the elastically and quasi-elastically scattered electron. In practice, the ZLP will always have a slight broadening and is primary due to the energy spread inherent in the electron source. The full width half-maximum (FWHM) of the ZLP is taken as a measure of the spectral resolution, which is normally in the range of ~ 0.3 eV to 2.0 eV, depending on the electron emitter and possible monochromator. The spectral resolution determines how well two spectral signals can be separated. For specimen with a thickness less than the mean free path of inelastic scattering (roughly 100 nm for 100 keV [46]) the ZLP will be the most intense feature in the EEL spectrum.

The CL region represents the excitation of the electrons localized in the inner-shells of the specimen. Here, the electron is excited from a core state to an unoccupied state above the Fermi level, leaving the atom ionized. These excitation are exhibited as ionization edges in the EEL spectra, as illustrated in the CL spectrum in Figure 19, and mirror the binding energy of the corresponding atomic shell. Since the binding energy is highly depending on the atomic number of the scattered atom, the ionization edges reveal information of which elements are present in the specimen [45]. Furthermore, the intensity of the ionization edge is proportional to the number of atoms contributing to the edge and scales by the inelastic partial cross-section of the atoms. Hence, this technique can be used for quantitative analysis of the elements in the specimen. On top of the main basic atomic edge
shape are oscillations that often is refereed to as fine structure. The fine structure of the edge is strongly depended on either bonding, coordination or nearest neighbour distance [47]. By analysis of the fine structure valued information on ionic charge, bonding or coordination can be extracted.

The ionization edges are superimposed on a downward sloping background, which arises from excitation of electrons of lower binding energy. Here, the largest contribution to the background arises from the plasmon peak. For thicker specimen, a contribution from plural scattering events will arise from multiple valence excitations. This background must be removed before quantitative analysis can be performed. That is achieved by fitting the spectrum prior to the ionization edge with an inverse power-law, i.e. $A E^{-r}$, where $E$ is the energy loss, $A$ and $r$ are constants. The power-law is then extrapolated beyond the ionization edge and subtracted from the spectrum, leaving only the ionization edge behind. The detailed description of the fitting procedure will be given for each individual case, later on in the thesis (Chapter 4 and Chapter 5).

2.5 SUMMARY

The chapter has introduced the basic concepts necessary to follow the work presented along this thesis. The chapter started by introducing the concepts of transmission electron microscopy, the construction of the instrument and how it utilizes an electron probe to obtain micrographs with atomic resolution of nanostructure such as heterogeneous catalyst. That was followed by a description of the in situ concept and how to obtain such in situ conditions within the TEM microscope by introducing the differentially pumped microscope and the closed window cell, known as the NR. The chapter was finalized by a description of MS and EELS, which helps providing chemical information about the exit gas and the specimen, respectively.
This chapter will address the aspect of how to achieve high-resolution TEM images of a specimen immersed in a gas. The chapter presents a comparison between the differentially pumped microscope and the NR system. The work presented in this chapter has been conducted in a collaboration with people from Thermo Fisher Scientific, and is at the moment in the drafting process for publication, listed as paper C in the publication list.
3.1 INTRODUCTION

The performance of in situ TEM has led to a vast number of reports, announcing new information about atomic dynamics at gas-solid interfaces, as reviewed by, e.g. [24, 48–50]. In contrast, only a few studies have reported on the effect of electron-gas scattering on image formation. Both elastic and inelastic processes have been suggested to cause degradation of the resolution [21, 51–54]. Common for those effects is the belief that the deterioration of the resolution was signal dependent and thus sensitive to that accumulated electron dose.

Recently, a number of studies have reported on the image resolution for solids immersed in a gas environment and have experimentally confirmed a signal-dependent resolution [24, 55, 56]. Interestingly, the studies further reported on a total electron dose rate dependency when monitoring the image resolution as a function of the pressure [24, 26, 55, 56]. These findings reveal that the image resolution not only depends on the accumulated number of electrons, but also on how the electrons are delivered. This implies that the intrinsic excitation of the gas-specimen system by the electron beam plays an essential role in achieving HRTEM images.

Before going any further, it should be mentioned that caution must be taken when using the term electron dose rate as it is vaguely defined in the literature. Here, the terminology from Ek et al. [26] is adopted.

<table>
<thead>
<tr>
<th><strong>Total electron dose rate</strong></th>
<th>The number of incoming electrons per unit time. It is denoted by the unit ( \text{[e}^{-}/\text{s}] ) or ([\text{nA}]).</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Areal electron dose rate</strong></td>
<td>The number of incoming electrons per unit area per unit time. It is denoted by the unit ( \text{[e}^{-}/(\text{Å}^2\text{s})] ).</td>
</tr>
<tr>
<td><strong>Accumulated electron dose</strong></td>
<td>The number of incoming electrons per unit area. It is denoted by unit ( \text{[e}^{-}/\text{Å}^2] ).</td>
</tr>
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</table>

One hypothesis, first presented by Jinschek and Helveg [24], was that the total electron dose rate dependency on the image resolution was attributed to the inelastic interaction between the primary electrons and the gas molecules. This suggestion is consistent with the findings of a more pronounced total electron dose rate dependency for an Au/C specimen (Agar S106) immersed in \( \text{N}_2 \) compare to \( \text{H}_2 \) [24], where \( \text{N}_2 \) has a larger total ionization cross-section \( \sigma_{\text{RBE}}(\text{N}_2, 300\text{keV}) = 1.20 \times 10^{-2} \text{Å}^2 \) than \( \text{H}_2 \) \( \sigma_{\text{RBE}}(\text{H}_2, 300\text{keV}) = 3.16 \times 10^{-3} \text{Å}^2 \), here using the relativistic binary-encounter-Bethe formula [57, 58]. The hypothesis was further strengthened as the dependency was more
distinct for a primary electron energy of 80 keV compared to 300 keV, again corresponding to a higher inelastic scattering cross-section [24].

In the report of Ek et al. [26], the effect of the specimen itself on the resolution degradation was studied. Here, it was reported that a higher tolerance to the total electron dose rate was observed, in terms of resolution degradation, on a SiC film in a MEMS device (Protochips Aduro [59]) compared to the Au/C specimen (Agar S106). Moreover, the tolerance of the total electron dose rate was increased when the SiC specimen was elevated from 40°C to 400°C [26]. These findings can be explained by an increase in electrical conductivity between the specimens and upon heating, where a decrease in electrical resistivity from 12 kΩ to 7 kΩ was reported for the latter [26]. An increase in electrical conductivity will improve the de-charging of the specimen and thus reduces the charge that builds up under the electron beam. These findings give further support to the hypothesis raised by Jinschek and Helveg, suggesting that charging may induce specimen movement generated by a capacitive effect between the individual parts of the specimen [24].

Until now, the total electron dose rate dependency on the image resolution has only been studied using the differentially pumped system. In this chapter, the investigation is taken further to include the NR system. Here, it is demonstrated how the NR system tolerates much higher total electron dose rates, even at higher pressure, while sustaining the intrinsic microscope resolution.

3.2 Method

The image resolution limits were examined by adopting the procedure reported in the previous studies [24, 26]. Here, the resolution limit was defined as the highest spatial frequency, which could be associated to the specimen lattice spacing, present in the image at each specific condition. The spatial frequencies in the image were determined from the fast Fourier transform (FFT) of the image. This method provides an easy and relatively fast way to estimate the image resolution at varying conditions. However, it should be stressed that this is only an estimate, as the observed image resolution cannot be directly equated with the information limit. Because of the crystalline orientation of the specimen, the size of the NPs or lack of significant SNR, it might be possible to resolve higher spatial frequencies than what is observed in the experiment. On the other hand, a HRTEM image is constructed of both linear and non-linear contributions, where the latter are not directly related to the specimen. These non-linear components can generate FFT contributions with higher spatial frequencies, resulting in an overestimation of the information
limit [60]. However, at higher primary electron energy (300 keV) these non-linear contributions are less pronounced [60].

A more recognized method to estimate the resolution limit is the Young’s fringes method, even though that the method is not fully valid either [60]. The Young’s fringe test is based on the FFT of an amorphous specimen, from which the highest frequency is identified. To discern the signal form the detection noise, two images acquired with a slight real-space displacement is added prior to the FFT. As a result, a Young’s fringe pattern appears in the diffractogram from which the signal can be distinguished from the detection noise. To address the validity of the adopted lattice fringe method, additional measurements were conducted using the Young’s fringe method for comparison between the two methods.

The variation in total electron dose rate was controlled by changing the second condenser aperture. For each setting of the total electron dose rate, the illumination area was adjusted to accomplish a constant areal electron dose rate of $1500 \text{ e}^-/(\text{Å}^2 \text{s})$ to $1600 \text{ e}^-/(\text{Å}^2 \text{s})$ by changing the position of the beam cross-over between the second and third condenser lenses. At each setting, the total and areal electron dose rate, together with the illumination area, were monitored by the pre-GIF CCD camera. This was accomplished by recording the entire beam at the CCD camera in vacuum without any specimen in the field-of-view. The total electron dose rate was calculated using the summed intensity from the whole image. By dividing the total electron dose rate by the measured illumination area, the areal electron dose rate was calculated. The CCD camera was calibrated prior to the experiment by trapping the entire beam in the drift-tube (like a Faraday-cup) while measuring the output current. That results in a conversion factor of $2.8 \text{ counts/e}^-$ and was used to calculate the electron dose rates. For the calibration of the CCD camera pixel size at the lower magnifications, a Mag*I*Cal standard grid was utilized.

All images were recorded with an exposure time between 0.85 s to 1.5 s, resulting in an accumulated electron dose beyond 1000 $\text{ e}^-/\text{Å}^2$, which is required to obtain HRTEM lattice fringes. Also, all images were acquired at a fixed CCD pixel size of 0.0237 nm and was calibrated towards the spacing of Au lattice fringes observed in vacuum, such that the Nyquist criteria was fulfilled at the inherent resolution limit. Furthermore, the pre-specimen beam blanker was used to record the images, meaning that the electron beam only is present on the specimen and gas system during the actual image acquisition. That is beneficial because the image resolution has been reported to degraded over time when the specimen and gas system are contentiously illuminated by the electron beam [26].

All present data were acquired at RT.
Figure 20: Overview of the particle coverages of the nanoreactor windows upon loading. 

A TEM image of an entire window from the Thermo Fisher NR loaded with Au. B Displays a high-magnification HRTEM image of the Au particles. C TEM image of an entire window from the Dimes NR loaded with Pt. D Displays a high-magnification HRTEM image of the Pt particles.

3.2.1 Specimen Preparations

For the comparison between the Young’s fringe and the lattice fringe method, an amorphous Ge thin-film was employed, sputter coated with Au islands of approximately 6 nm thickness, measured by quartz crystal microbalance (QCM) [61] during the sputter coating process. Here, the amorphous Ge thin-films deliver a relatively heavy scattering suitable for Young’s fringe testing. Meanwhile, the Au islands deliver stable crystalline areas appropriate for obtaining lattice fringes.

For the study of the image resolution within the differentially pumped system, a 30 nm thin amorphous Si₃N₄ membrane (Agar S171-1) is employed. The Si₃N₄ membrane is sputter coated with Au islands with a thickness of around 8 nm to 9 nm, measured by QCM [61]. Here the Au islands deliver crystalline areas suitable for the investigation of the image resolution. That makes a direct comparison pos-
sible between the NR and the differentially pumped system in terms of material, thickness and gas pressure.

To investigate the image resolution within the NR system, two different NRs are employed, loaded with Au and Pt NPs, respectively. The first is a Thermo Fisher reactor equipped with a gas channel height of 2 µm and loaded with Au NPs. Here, the Au NPs were synthesized beforehand (NanoXact, 15 nm) and dissolved in n-hexane. The solution was loaded into the NR by drop cast on the inlet connection, according to the procedure given in Section 2.2.4. Meanwhile, a Dimes reactor equipped with a channel height of 5 µm was loaded with Pt NPs. Here, the Pt NPs were synthesized inside the reactor from a salt solution of tetraammineplatinum(II)nitrate in water. The salt solution was drop cast at the inlet connection of the reactor, similar to the description above. After the loading process, the Pt NPs were calcinated inside the microscope at 200 mbar of O₂ at 500 °C to break down the tetraammineplatinum(II)nitrate to PtO. Finally, the PtO was reduced to Pt NPs in 1 bar of H₂ at 300 °C.

Figure 20 displays the loading of the NPs inside the two NRs. Figure 20 A displays an overview of the Thermo Fisher reactor window, illustrating the coverage of Au NP. Figure 20 B depicts a HRTEM image of the Au NPs from the same window. Similar overview of the Dimes reactor loaded with Pt is shown in Figure 20 C and a zoom-in on the Pt NPs is displayed in Figure 20 D.

3.3 LATTICE FRINGES VERSUS YOUNG’S FRINGES

To validate the adopted method [24, 26], a comparison of the lattice fringe and the Young’s fringe method is performed. Figure 21 A displays a TEM image of the specimen in vacuum, constructed by superimposing two separate TEM images with a real-space displacement of around 2 nm, and its FFT, showing the Young’s fringe pattern as the periodical lines and the spatial frequencies associated with the lattice fringes in the real-space TEM image. The TEM images are recorded using an areal electron dose rate of 1600 e⁻/(Å² s) with an exposure time of 1.5 s, resulting in an accumulated incoming electron dose of 2400 e⁻/Å.

For high-end electron microscopes with an inherent information limit close to the physical limit of resolution (0.5 Å, the Bohr radius), the condition of the specimen can suddenly become a limiting factor for the performance. This fact is demonstrated in Figure 21 A, where neither the lattice fringe method nor the Young’s fringe method meet the inherent resolution limit of the microscope. This might be cause of the thickness of the Ge thin-films, which at the time of writing is unknown, resulting in too low an accumulated electron dose to obtain higher spatial resolution. Additional measurement has indicated that this could indeed be the case since a longer exposure time increased
Figure 21: Comparison of the resolution limit between the Young’s fringes and the lattice fringes methods. A Displays a superimposed TEM image of the Au/Ge specimen, generated from two images acquired with a slight real-space distance of 2 nm between them, and its FFT, illustrating the Young’s fringe pattern as well as spacial frequencies related to the lattice fringes in the TEM image. B The displays show the FFTs of superimposed TEM images recorded on the Au/Ge specimen immersed in 1 mbar and 10 mbar of N₂ as a function of the total electron dose rate. For all FFT displays, the image resolution is denoted for each condition (upper right corner) and corresponds to the highest spatial frequency present in the image (indicated by the white circles). The superimposed red circles indicate the extension of the Young’s fringe pattern. All displays are acquired with an areal electron dose rate of 1600 e⁻/(Å² s) and an exposure time of 1.5 s.
the resolution limit in the images. However, the goal of this specific examination is not to push the image resolution to the information limit, but rather to compare the resolution limit across the two methods. That is still doable, even though the image resolution does not match the inherent microscope information limit.

In the FFT display shown in Figure 21 A, the highest spatial frequency present, which can be associated with the lattice parameter of Au is denoted in the upper right corner and is further indicated in the display by the superimposed white circles. Furthermore, the extension of the Young’s fringes is indicated by the red circle superimposed on the FFT display and is determined from visual examination of the Young’s fringe pattern. In general, the Young’s fringe pattern demonstrates a non-uniform extension, where the extension seems to propagate to high spatial frequencies along the parallel direction of the pattern compared to the perpendicular direction. This variation is most likely caused by vibration along the direction of the sample holder. Using the extension along the parallel direction of the pattern demonstrates a slightly lower resolution limit than the 1.23 Å observed with the lattice fringe method in vacuum (Figure 21 A).

Figure 21 B shows the results for the Au/Ge specimen immersed in a N₂ environment using the differentially pumped system. Here, the FFTs are acquired with a total electron dose rate of 0.5 nA, 1.1 nA and 2.5 nA, respectively, for an environmental pressure of 1 mbar and 10 mbar. For the FFTs acquired within 1 mbar of N₂, it is seen that the resolution limit measured by the lattice fringe method has dropped from 1.23 Å in vacuum to 1.44 Å, where it remains unaffected by the total electron dose rate. A similar analysis using the Young’s fringe method reveals an identical resolution limit for 1 mbar as for vacuum, which is around 1.44 Å. This level is sustained along with the variation of the total electron dose rate and is consistent with the findings from the lattice fringe analysis. Increasing the pressure to 10 mbar reveals an image resolution of 1.44 Å for a total electron dose rate of 0.5 nA. As the total electron dose rate is increased to 1.1 nA and 2.5 nA, the resolution drops to 2.35 Å where it remains. The findings are identical for both methods.

Both methods demonstrate degradation in the image resolution as a function of the pressure and the total electron dose rate, which is in agreement with previous reports [24, 26, 55, 56]. Overall, the two methods show great consistency with a small exception for the recording performed in vacuum, where the lattice fringe method reveals a slightly higher resolution than the Young’s fringe method. Since the following experiments mainly are performed within a gaseous environment, it is concluded that the lattice fringe method is valid for estimating the image resolution limit.
Figure 22: Image resolution for Au/Si$_3$N$_4$-specimen immersed in 5 mbar N$_2$ as a function of total electron dose rate. The displays show FFTs of high-resolution TEM images of Au NPs sputtered on a 30 nm thick Si$_3$N$_4$ membrane. The image resolution is denoted for each condition (upper right corner) and corresponds to the highest spatial frequency in the image (indicated by the red circle). Lower spatial frequencies present in the image are marked by white circles. The display at the left demonstrates the corresponding image resolution acquired in vacuum at the high total electron dose rate (2.9 nA). All displays are acquired with an areal electron dose rate of 1.600 e$^-$/($\mu$m$^2$).

3.4 Resolution within the Differentially Pumped System

Figure 22 displays TEM images of the Au/Si$_3$N$_4$ specimen together with their corresponding FFTs, as a function of the total electron dose rate. Here, the left image is recorded in vacuum, using a total electron dose rate of 2.9 nA, whereas the images to the right are recorded in 5 mbar of N$_2$, using a total electron dose rate of 0.3 nA, 1.2 nA and 2.9 nA, respectively. All images are acquired with an areal electron dose rate of 1.600 e$^-$/($\mu$m$^2$) and an exposure time of 1.5 s, corresponding to an accumulated electron dose of 2400 e$^-$/($\mu$m$^2$). Beneath each image, its corresponding FFT is located. In each FFT, the image resolution is denoted in the upper right corner, which corresponds to the highest spatial frequency present in the FFT and is indicated by the red circle superimposed on the FFT. All other spatial frequencies present in the image, which can be associated with the lattice spacing of Au, are indicated by superimposed white circles.

From the FFT acquired in vacuum, it reveals an initial image resolution of 1.02 Å, corresponding to the (400) reflection of Au. When introducing the N$_2$ into the e-cell, the image resolution starts to deteriorate as a function of the total electron dose rate. Here, the image resolution is 1.44 Å at the lowest total electron dose rate, corresponding to the (220) reflection. At the intermediate total electron dose rate,
the image resolution is already degraded to 2.35 Å (111 reflection), whereas all spatial frequencies are lost at the highest value of the total electron dose rate.

That is consistent with the tendencies from previous reports [24, 26, 55], however, the image resolution seems to be less tolerant to the total electron dose rate compared to previous reports on Au/C, Si, and SiC specimens [26, 55]. Still, that might be expected due to the electrical properties of the specimen material. As Si₃N₄ is distinguished as an insulating material, the electrical conductivity of the Si₃N₄ membrane is expected to be relatively low, resulting in deterioration of the discharging of the Si₃N₄ membrane. Consequently, charges will build up faster under the illumination of the electron beam. In continuation of the hypothesis suggested by Jinschek and Helveg [24] and concurred by Ek et al. [26], such charging may induce specimen movements mediated through capacitive effects between the individual parts of the specimen and resulting in the degradation of the image resolution.

3.5 Resolution within the Nanoreactor System

The influence of the total electron dose rate on the image resolution in the NR system is elucidated in Figure 23. Here, the image resolution limits were estimated from Au islands loaded into a Thermo Fisher NR while exposed to a flow of N₂ gas with a pressure in the reactor zone of 5 mbar and 1000 mbar, respectively. Figure 23 shows the FFTs of the images acquired from the NR as a function of the total electron dose rate. All images are recorded at similar conditions of total and areal electron dose rate, and exposure time as for the examination of the Au/Si₃N₄ specimen presented above in Figure 22.

In 5 mbar of N₂, the image resolution seems to be unaffected and maintains a resolution of 0.91 Å, corresponding to the (331) reflection, for all three settings of the total electron dose rate. Even the intensity of each individual reflection looks to be sustained along with the increase of total electron dose rate. When the pressure is increased to 1000 mbar, the resolution drops slightly to 1.02 Å, corresponding to the (400) reflection, where it is unchanged as a function of the total electron dose rate. However, spatial frequencies higher than 1.02 Å are observed for a total electron dose rate of 0.3 nA and 1.2 nA and are indicated by the small red circles superimposed in the FFTs. These frequencies cannot directly be associated to the lattice spacing of Au and thus they are treated as originating from multi-scattering.

These findings imply that the NR system holds a much higher tolerance toward the total electron dose rate as no degradation of the resolution is observed while increasing the total electron dose rate. This holds for both low (5 mbar) and high (1 bar) pressures.

Next, the influence of the gas type is investigated by employing a Dimes reactor loaded with Pt NPs. Here, images are recorded with
Figure 23: Image resolution for an Au-loaded Thermo Fisher nanoreactor exposed to N₂ as a function of total electron dose rate. The displays show FFTs of HRTEM images acquired with an areal electron dose rate of 1600 e⁻/(Å²·s). The image resolution is denoted for each condition (upper right corner) and corresponds to the highest spatial frequency in the image associated with the Au (indicated by the red circle). Lower spatial frequencies associated with the Au lattice spacing are marked by white circles if they appear in the FFTs. The lower displays show the image resolution with a pressure of 5 mbar in the reactor zone, where the upper displays are acquired at pressure of 1 bar.

A total electron dose rate of 5.4 nA, an areal electron dose rate of 1500 e⁻/(Å²·s), and an exposure time of 0.85 s, while flowing 1 bar of gas through the reactor zone. The images are shown in Figure 24, where also their corresponding FFTs are displayed. In Figure 24, the left image and corresponding FFT illustrate the image resolution for the Pt NPs recorded in vacuum, while the remaining images and FFTs (to the right) demonstrate the image resolution during the exposure to N₂, O₂, and Ar, respectively. Here, N₂ and Ar is regarded ad inert gasses, where Ar has a significantly higher inelastic cross-section compared to N₂ [57, 58]. In contrast, O₂ is considered as a reactive gas and has an inelastic cross-section in-between N₂ and Ar.

Form the acquisition in vacuum, an initial image resolution of 0.98 Å is observed, corresponding to the (400) reflection of Pt. Besides, all lower ranked reflections for Pt are present in the FFT. When the initial image resolution recorded in vacuum is compared to the image resolution acquired with 1 bar of N₂ flowing through the NR, no considerable changes are observed. The same is true for recording in O₂ and Ar, where an image resolution of 0.98 Å is maintained.
From the FFTs acquired with O₂ or Ar presented in the reactor, it is observed that some of the lower spatial frequencies are missing compared to the FFTs recorded in vacuum or N₂. These, however, are a token of the local variation of the specimen as not all areas provide the required orientations, sizes or loadings of NPs to achieve all spatial frequencies in one single image. The absence of these lower spatial frequencies is therefore not caused by the electron-gas interactions, but is due to the local condition of the specimen.

3.6 Discussion

It is shown that the NR systems offer a high tolerance toward the total electron dose rate compared to the differentially pumped system. Where the image resolution in the differentially pumped system begins to deteriorate at a total electron dose rate of 0.3 nA in 5 mbar of N₂, the NR system sustains an image resolution of 1 Å toward a higher total electron dose rate (5.4 nA) at a higher pressure (1 bar) in a gas with a higher inelastic interaction cross-section (Ar).

Comparing the specimen used in Figure 22 and the NR system used in Figure 23, the specimens are considered similar in terms of materials, thickness, gas, and pressure. That leaves the gas height as the main difference between the two systems. For the NRs, the gas height is within the µm-regime, which means that the amount of gas that the electron beam sees is dramatically reduced. In Section 2.2.3,
the gas height was related to an equivalent solid thickness, trying to give a perspective on the gas phase influence on the electron scattering. However, in that consideration, only the height of the gas phase is considered, neglecting any properties of the gas types. Another way to address this is to consider the number of extrinsic scattering events in the gas phase, described as the number of scattering centers in a cylindrical volume defined by the cross-section $\sigma$ and the travel distance $L$, being the height of the gas phase [62]. Hereby, the gas properties in terms of the inelastic cross-section is included in the considerations. For an ideal gas, the number of extrinsic scattering events are given as:

$$m = \frac{LPM\sigma}{k_BT}$$

(17)

where $P$ denotes the pressure, $M$ the number of atoms the gas molecule consists of, $k_B$ Boltzmann’s constant and $T$ the temperature. If focusing on the inelastic scattering only, using the relativistic binary-encounter-Bethe model ($\sigma_{\text{RBEB}}(N_2, 300 \text{ keV}) = 1.20 \times 10^{-2} \text{ Å}^2$) [57, 58], the number of extrinsic scattering for 5 mbar in the differentially pumped system becomes $2.16 \times 10^{-1}$ events. For the NR system with a gas channel height of 2 $\mu$m, the same number is only $1.46 \times 10^{-4}$ event and becomes $2.91 \times 10^{-2}$ event as the pressure is raised to 1 bar. This implies that the inelastic scattering between the primary electron and the gas molecules is reduced considerably when going from the differentially pumped system to the NR system.

Another aspect worth considering is the structure of the specimens and in particular the membranes itself. For the specimen used in the differentially pumped system, the 30 nm thick membrane is suspended over a 200 $\mu$m thick support frame in which a 0.5 $\text{mm} \times 0.5 \text{mm}$ hole is located in the center, exposing the $\text{Si}_3\text{N}_4$ membrane. In contrast, the NR windows are only 4 $\mu$m to 6 $\mu$m in diameter and are etched directly in the 1 $\mu$m thick membranes enclosing the gas. Thus it is plausible that the NR windows appear more rigid and stable than the 0.5 $\text{mm} \times 0.5 \text{mm}$ suspended membrane for the conventional specimen. If the image resolution is deteriorated due to induced specimen movement mediated through a capacitive effect as suggested by Jinschek and Helveg [24], then the NR system will perform best due to their more rigid and stable windows, which indeed is the case.

3.7 conclusion

The present chapter has demonstrated how the image resolution can be sustained at the inherent microscope resolution at ambient pressure. The findings indicate that the NR system provide a higher tolerance toward the total electron dose rate in terms of image resolution compared to what is observed in the differentially pumped system.
The findings also imply that the image resolution was indifferent of
the gas type, which goes against previous findings from the differenti-
tially pumped system [24]. Finally, the lattice fringe method was com-
pared to the more recognized Young’s fringe method, which reveals
similar results for the two methods within the differentially pumped
microscope.
In the previous chapter, it was demonstrated how the NR makes its mark in terms of facilitating high-resolution performance while operating at ambient pressure and how it outperforms the differential pumped microscope, even at low pressures. The fact that the NR performs better in terms of resolution does not necessarily imply that it performs better in terms of beam induced effects.

Nobody has, however, addressed the integrity of the NR windows. This chapter is therefore dedicated to address the integrity of the NR windows while operating at an oxidizing environment. The work present in this chapter has been conducted in close cooperation with former Master student at Haldor Topsoe A/S and current PhD student at DTU Physic, Hjalte Rørbech. The work presented is in preparation for publication and is listed as paper B in the publication list.
4.1 INTRODUCTION

In Section 2.2.2, it was documented how silicon and MEMS technology have been utilized to fabricate closed window cells, which facilitates studies at high pressure and temperatures. Today, a vast number of closed window cells utilize amorphous SiN as window materials [33, 35, 63]. This is due to relatively light scattering of the electrons within the SiN window materials, whereas also the amorphous structure is beneficial for suppressing scattering. Besides, the use of SiN is based on a common assumption that the SiN windows are chemical inert against the conditions used within the reactor such as catalytic research (i.e. meaning that the window materials stays unchanged in the reaction). This assumption stems from the microelectronics industry, where amorphous silicon nitride is widely used due to its chemical stability, high structure density and its dielectric properties [64, 65]. Besides, chemical vapor deposited silicon nitride is often used as masking and passivating layer cover for semiconductor devices [65], e.g. in connection with oxidation processes of silicon [66]. However, silicon nitride is thermodynamic unstable when exposed to an oxidizing environment [65, 67, 68]:

\[
\text{Si}_3\text{N}_4 + 3\text{O}_2 \rightleftharpoons 3\text{SiO}_2 + 2\text{N}_2; \quad \Delta H_{298\,\text{K},1\,\text{bar}} = -1922 \text{ kJ mol}^{-1}
\]  

That is problematic since many catalytic reaction proceed in an oxidizing conditions, e.g. calcination [69]. On top of it comes that the windows need to withstand the exposure of the electron beam.

Consequently, this chapter will challenge the common assumption, that the NR windows is chemical inert, by addressing the window integrity. That is carried out by seeking answer to the following question: i) are the silicon-based windows stable under oxidizing conditions and if not, is it then thermally driven or induced by the electron beam, and ii) how do the operational conditions (pressure and temperature) and the illumination conditions (the areal electron dose rate and the primary electron energy) influence on the integrity of the NR windows.

4.2 METHOD

To study the integrity of the Si-based window cells, a Dimes NR with a gas height of 5 µm was employed. The NR was inserted into the FEI Titan 80-300 ETEM microscope, where it was evacuated to base pressure of \(\leq 10^{-5}\) mbar. The integrity was studied while exposing the NR to an oxidizing environment (Alphagaz™ 1 oxygen, purity of 99.995 %), introduced through the inlet, meanwhile the outlet was directly connected to the mass spectrometer for gas composition analysis and was pumped by a TMP.
To address the integrity, the chemical composition of the NR windows were monitored by use of EELS and was acquired with the post-column GIF system while operating the microscope projector system in diffraction mode. An entrance aperture of 2 mm and a camera length of 60 mm was employed during the acquisitions, corresponding to a collection semi-angle of 22.1 mrad for a primary electron energy of 80 keV and 17.1 mrad for 300 keV, respectively. Prior to the experiment, the Cs-correction was tuned to a Cs-value of $-8 \mu m$ to $-25 \mu m$ using an Au/C cross grating grid (Agar S106), followed by a tuning of the GIF Tridiem in vacuum without any specimen in field-of-view. That results in a full-width at half maximum of the ZLP below 0.8 eV for electrons with a primary energy of 80 keV and 1.8 eV for 300 keV. While operating the GIF system in spectroscopy mode, the post-GIF CCD camera was operated with 2048 pixel and an energy dispersion of 0.2 eV/pixel. The energy dispersion was calibrate by help from external measurements on a BN specimen from GATAN, as discussed in Section 2.4.

Before and after each experimental series, a number of reference EEL spectra and TEM images were recorded at the evacuated base pressure. Here, the reference spectra include a LL spectrum of the ZLP, a CL spectrum of the Si-L$_{2,3}$ edge (99 eV) and the N-K edge (401.6 eV), and a CL spectrum of the N-K edge and the O-K edge (532 eV). In addition, a HRTEM image of the windows was recorded at high magnification, from which the defocus of each membrane can be determined and thus also the channel height.

To address the question about the integrity of the NR windows, two separate windows was examined while exposed to oxidizing conditions, i.e. meaning that O$_2$ was flowed through the reactor, leading to a pressure of 1 bar in the reactor zone. This was done for 30 min while the NR was heated to 500 $^\circ$C. The first window went unilluminated during the entire exposure period, while the second window was illuminated with an areal electron dose rate of 1000 e$^-/\AA^2\text{s}$ for the last 20 min of the exposure period. By comparison between the raw reference spectra acquired prior to and after the exposure period for the two windows, it was possible to address on the integrity of the NR window, and whether it was induce by the electron beam.

To further address the influence of the operational and illumination conditions on the integrity of the NR windows, an estimated level of oxidation was determined as the atomic ratio between the O and N species, which were extracted from the ionization edges. In order to extract the ionization signals, the background first has to be removed. This was done by fitting an usual power-law prior to the ionization edges according to the description in Section 2.4. For the N-K edge, a fitting window ($\gamma_N$) of 30 eV was used with an off-set value of 11.6 eV to the ionization edge, as illustrated in Figure 25. The similar values for the O-K edge was 30 eV for the fitting window ($\gamma_O$) and 10.0 eV.
Figure 25: Background fitting and subtraction of the electron energy-loss spectra recorded on the NR window during oxidation. The raw spectrum is represented by the blue curve. The background is fitted by a power-law prior to each ionization edge within the fitting window (γ) indicated by the dotted lines. The power-law is extrapolated beyond the ionization edges (back dashed lines) and subtracted, resulting in the signal of the ionization edges (red spectra).

for the off-set. The fitted power-laws were extrapolated to energy-losses beyond the N-K and the O-K edges (black dashed lines) and subtracted from the spectrum, revealing ionization signal (red solid curves), as illustrated in Figure 25. The integrated signals (\(I_N\) and \(I_O\)) were estimated by integrating from the N-K (401.6 eV) and the O-K (537.5 eV) and to 20 eV above. To determine the amount of the N and O species, the integrated signals were divided by the integrated cross-sections (\(\sigma_K\)) for the N-K and O-K, respectively. The integrated cross-sections were calculated with the SIGMAK3 program \(^1\), which employs a hydrogenic approximation and relativistic kinematics as described by [45]. From the extracted amount of N and O species within the illuminated area, the O/N ratio was calculated as an estimated level of window oxidation.

In order to determine the nature of the oxidation process, a fixed parameter space was established. From here, each of parameters was varied one at the time, such to establish the influence of each given parameter. For each variation of the fixed parameters, a series of measurements was acquired from which the progress of the oxidation level was estimated as a function of the accumulated electron dose rate, defined as the oxidation rate. The fixed parameter space was by the following parameters:

\(^1\) MATLAB source code for the SIGMAK3 program is obtain from https://sites.google.com/site/temsemeels/home/matlab-programs-from-eels-in-the-electron-microscope-3rd-edition
The fixed parameter space:

- Areal electron dose rate: $1000 \text{e}^-/(\text{Å}^2 \text{s})$
- Partial pressure of O\textsubscript{2}: 500 mbar
- Temperature: 500 °C
- Primary electron energy: 300 keV

4.3 The Integrity of the Nanoreactor Windows

Figure 26 displays the raw EEL spectra recorded prior to (blue spectra) and after (red spectra) the exposure to 1 bar of O\textsubscript{2} from two individual windows. The first window, which is represented by the EEL spectra in Figure 26 A-C, was unilluminated during the entire exposure period, whereas the other window, represented by the EEL spectra in Figure 26 D-F, was illuminated with an areal electron dose rate of $1000 \text{e}^-/(\text{Å}^2 \text{s})$ during the last 20 min of the exposure period. All spectra are recorded at evacuated state using an areal electron dose rate of $1000 \text{e}^-/(\text{Å}^2 \text{s})$.

Figure 26 A-C display the LL spectra of the ZLP and the plasmon peak, the CL spectra of the Si-L\textsubscript{2,3} edge and the CL spectra of the N-K and O-K edge for the NR window that stayed unilluminated during the entire period. Comparison between the spectra recorded before and after the exposure of O\textsubscript{2} demonstrates that there is an overall consistence between the spectra. Both the ZLPs and the plasmon peaks, displayed in Figure 26 A, are considered unchanged in their intensity and shape. The same goes for the Si edge in Figure 26 B, as well as for the N and O edges shown in Figure 26 C. That implies that the windows material is chemical resistance to the oxidation condition imposed on the NR, while staying unilluminated during the exposure process.

Figure 26 D-F display similar spectra recorded under identical conditions as earlier, but on another NR window, which was illuminated with an electron dose rate of $1000 \text{e}^-/(\text{Å}^2 \text{s})$ during the last 20 min of the O\textsubscript{2} exposure period. A comparison between the spectra recorded prior to and after the exposure of O\textsubscript{2} while illuminated demonstrates a radical difference in the spectra. In Figure 26 D it is observed that a slight broadening of the plasmon peak is occurring over the experiment. Also the position of the plasmon peak has shifted slightly towards higher energy-losses. The broadening is reflected into the CL spectra where the background intensity of the Si-L\textsubscript{2,3} edge is significantly heightened compared to the prior. Besides the upward shift in intensity, a modification of the Si-L\textsubscript{2,3} edge shape is observed. The observation reveals a shift of around 2 eV for the main peak (from
Figure 26: Electron energy-loss spectroscopy of the nanoreactor windows during exposure of $O_2$. The EEL spectra is recorded before (blue) and after (red) the exposure to $O_2$ for 30 min at 500°C. A-C display spectra for a window that is unilluminated during the exposure to $O_2$. D-E show similar spectra for another window, but where the window is illuminated for the last 20 min of the exposure to $O_2$. All spectra are recorded at evacuated state ($\leq 10^{-5}$ mbar) and at 500°C using an electron dose rate of $1000 \text{ e}^-/(\text{Å}^2 \text{s})$.

107.4 eV to 109.4 eV), meanwhile a pre-shoulder appears around an energy-loss of 106.4 eV. Also the fine structure around the peak at 177.6 eV seems to change slightly. Also the fine structure in the energy interval 111 eV to 120 eV seems to change slightly. Finally, but most notable is the difference in the N-K and O-K edges that are displayed in Figure 26 F. Here, a dramatically drop in the N-K edge intensity is observed, while the intensity of the O-K has increased significantly. Consequently, it implies that the window material has undergone an oxidation process.

The findings strongly indicates that the window material is vulnerable to the oxidizing conditions imposed on the NR while illumination by the electron beam. Moreover, the findings implies that the oxidation of the NR windows is catalyzed by the electron beam. If
4.4 Influence of the Operational Conditions

As it is shown that the NR windows are vulnerable to the oxidizing environment, the investigation will now turn towards the operational conditions and how they influence on the integrity of the NR windows.
First, the effect of the partial pressure of $O_2$ is investigated, and is illustrated in Figure 28. Figure 28 displays the oxidation level along four different measurement series recorded on each their separated windows during an exposure to 10 mbar, 100 mbar, 500 mbar, and 1000 mbar of $O_2$, respectively. The star points in Figure 28 represent the reference measurements recorded before and after the exposure period, and are all recorded at evacuated state.

The initial references (at zero accumulated electron dose) reveal that the initial levels of oxidation are similar for all four windows. As the $O_2$ is introduced to the NR, the level of oxidation starts to rise. Figure 28 demonstrates how the oxidation occurs in two regimes with different oxidation rate. Here, the oxidation rate within the first regime is significant higher than the oxidation rate of the second regime. Furthermore, the first regime is significant shorter than the second regime, where the first regime only accounts for the first 1000 $e^–/Å$, approximately.

From Figure 28 it is seen that a higher partial $O_2$ pressure give rise to a more rapid oxidation. This is observed for the oxidation in both regimes. Within the first regime, a significant larger oxidation is observed for a pressure of 1000 mbar compared to the other. Similarly, a pressure of 500 mbar cause a significant larger oxidation than for 100 mbar, which again cause a higher oxidation than for 10 mbar. The same tendency is observed for the second regime. If the oxidation...
levels in the second regime are approximated to a first order regression as a function the accumulated electron dose (neglecting the end reference), the oxidation rate of each series is obtained, defined as the slope. The oxidation rates for the four pressure series are displayed in Figure 29 and demonstrate a nicely linear dependency on the partial O\textsubscript{2} pressure.

Another effect of the pressure is seen in the final references, which generally show lower values than the end measurements performed with gas present in the reactor. This difference appears to be depending on the pressure, i.e. a higher pressure leads to a larger drop. For the series recorded at 1000 mbar the drop is relative large, whereas no direct difference is observed for the series recorded at 10 mbar. However, a possible explanation is revealed if the EEL spectra themselves are examined.

Figure 30 displays the background subtracted EEL spectra of the O-K edge for the end measurement and the final reference from the 1000 mbar and the 10 mbar series, respectively. The CL spectrum recorded with 1000 mbar of O\textsubscript{2} present in the reactor reveals that two O-K edges are present; one at 532 eV, associated with the O\textsubscript{2} in the gas phase, and another around 537.2 eV, which is related to the solid O from the oxidation of the NR window. That is verified by consulting the reference spectrum acquired after the NR is evacuated for O\textsubscript{2}, where the O-K edge at 532 eV is vanished. Meanwhile, the O-K edge associated with the solid O is still present, however, its intensity has dropped considerably compared to the prior recording. That indicates that the O-K edge associated with the gas phase is convoluted with the O-K edge belonging to the solid O, which eventually will

Figure 29: The rate of oxidation of the nanoreactor windows as a function of the O\textsubscript{2} pressure. Displays the oxidation rate for the four pressure series displayed in Figure 28, revealing a linear relationship between the pressure of O\textsubscript{2} and the oxidation rate of the NR windows.
raise the intensity level of the latter as long as gas is present in the reactor. As the pressure is lowered, the O-K gas edge will decrease and its contribution to the solid O-K edge is reduced. That is exactly what are seen for the spectrum in Figure 30 recorded with an O\textsubscript{2} pressure of 10 mbar. Here, the O-K gas edge becomes undetectable, resulting in no visible difference between the end recording and the final reference spectra. This effect will eventually also influence the rapid oxidation seen in the first regime in Figure 28, where the largest effect will be for the 1000 mbar series, whereas the effect in the 10 mbar series most likely will be negligible.

To deconvolute this effect of the gas signal, an ideal approach would be to fit the O-K gas signal (using the main peak within the interval 532 eV to 535 eV) to a reference spectrum acquired of O\textsubscript{2} gas only, followed by a subtraction the fitted O-K gas signal from the main spectrum. However, at this time of writing, such gas reference spectrum has not yet been acquired. Instead, to elucidate the extend of the effect, the oxidation level is offset by a constant, such that the last recording (with gas in the reactor) and the final reference (at evacuated state) obtain the same value. The result is depicted in Figure 31. Figure 31 demonstrates that the correction lowers the oxidation within the first regime considerably. However, the oxidation is still more rapid than in the second regime. Moreover, the oxidation in the first regime still seems to be dependent on the pressure itself, with a higher oxidation for higher pressures.

The investigation will now turn towards the influence of the second operational parameter, namely the temperature. Figure 32 displays the influence of the temperature on the oxidation process for three series of 30°C, 100°C and 500°C, respectively. Each series are
Figure 31: Influence of the partial O$_2$ pressure on the integrity of the nanoreactor windows after correction of the O$_2$ gas peak convolution. The oxidation levels are displayed versus the accumulated electron dose illuminated at the NR window, while exposed to a partial O$_2$ pressure of 10 mbar, 100 mbar, 500 mbar, and 1000 mbar, respectively. Data are recorded at 500 °C using an areal electron dose rate of 1000 e$^{-}$/Å$^2$/s with a primary energy of 300 keV. Starts represent reference measurements recorded at evacuated state (≤10$^{-5}$ mbar). The data in regime 2 have been offset by a constant value, such to match the final reference point.

The initial references in Figure 32 reveals a considerable variation in the initial oxidation level compared to the measurements presented in Figure 28. Nevertheless, Figure 32 also demonstrates that two oxidation regimes exist, where the oxidation in the first is more rapid than for the second regime. This is valid for both the corrected and uncorrected data. However, the series at 100 °C does not show any direct oxidation with regime 1, as the other two series. Furthermore, the series do not demonstrate any difference between the last measurement with gas present in the reactor and the final reference recorded at evacuated state, as it is seen for the other series. Therefore, it is reasonable to suspect that something might have influenced the measurements of the series and thus, it would be beneficial to redo this particular series to be sure.

If the oxidation rates in the second regime are attained for the three series, determined by linear regression, the results demonstrate that the lowest oxidation rate belongs to the series at 500 °C with an oxidation rate of 8.52 × 10$^{-7}$ (e$^{-}$/Å$^2$)$^{-1}$, where the highest is obtained at 30 °C of 1.62 × 10$^{-6}$ (e$^{-}$/Å$^2$)$^{-1}$. Moreover, the oxidation rate for
Figure 32: Influence of the temperature on the integrity of the nanoreactor windows. The oxidation levels are displayed before (solid color) and after (faded color) the correction of the O\textsubscript{2} gas peak convolution versus the accumulated electron dose illuminated at the nanoreactor windows, while heated to a temperature of 30\textdegree C, 100\textdegree C, and 500\textdegree C, respectively. The data are recorded with an areal electron dose rate of 1000 e\textsuperscript{−}/(Å\textsuperscript{2}s) and a primary energy of 300 keV, while being exposed to 500 mbar of O\textsubscript{2}. Starts represent reference measurements recorded at evacuated state (≤10\textsuperscript{−5} mbar).

100\textdegree C (1.61 × 10\textsuperscript{−6} (e\textsuperscript{−}/Å\textsuperscript{2})\textsuperscript{−1}) is very similar as to the oxidation rate of series acquired at 30\textdegree C.

4.5 INFLUENCE OF THE ILLUMINATION CONDITIONS

In the following, the influence of the illumination condition is considered. These are parameters that refers to the operation of the microscope, and should be adjusted to the experiments, such that the studied reactions are not affected by the illumination conditions, as discussed in Section 2.1.4. However, it is difficult to predict the influence of the illumination condition and thus, it must be experimentally investigated. In this section, the areal electron dose rate and the primary electron energy will be examined to determine how they influence in the integrity of the NR windows.

First, the effect of the primary electron energy is addressed. Figure 33 displays two series acquired from separated windows with a primary electron energy of 80 keV and 300 keV, respectively. Figure 33 demonstrates the oxidation level of the windows before (solid color) and after (faded color) the correction for the gas convolution effect.
4.5 INFLUENCE OF THE ILLUMINATION CONDITIONS

Figure 33: Influence of the electron energy on the integrity of the nanoreactor windows. The display shows the oxidation levels as a function of the accumulated electron dose illuminated on the NR windows, using a primary electron energy of 80 keV and 300 keV, respectively. The data is recorded with an areal electron dose rate of $1000 \text{ e}^-/(\text{Å}^2 \text{s})$ while exposed to an $O_2$ pressure of 500 mbar at 500 °C. Starts represent reference measurements recorded at evacuated state ($\leq 10^{-5}$ mbar).

The initial references reveals a considerable difference in the initial oxidation level for the two windows. Despite this, the oxidation within the first regime seems to be relative similar for the two series before the gas convolution correction. If the measurements are corrected for convolution of the gas peak, its is clear that the correction for the 80 keV series fails, as the correction offsets the series to a starting level below the level of the initial reference, which obviously is not valid. The reason for this is that the correction method builds on the validity of the final reference. In Figure 33, the 80 keV series demonstrates a significant larger variation between the end measurement with gas in the reactor and the final reference compared to any of the other series. The reason might stem from specimen drift during the gas evacuation of the NR. Specimen drift will lead to a shift of the probing area toward areas that have not undergone any oxidation and hence result in a lower measured level of oxidation.

If the oxidation rates are determined within the second regime, using a first order regression, it is revealed that a more rapid oxidation is taking place with a primary electron energy of 80 keV than for 300 keV. Here, the oxidation rate is $1.35 \times 10^{-6} \text{ (e}^-/\text{Å}^2)^{-1}$ for 80 keV, where it is $8.52 \times 10^{-7} \text{ (e}^-/\text{Å}^2)^{-1}$ for 300 keV. Hence, the measurements implies that a lower primary electron energy accelerate the oxidation of the NR windows.
Next, the impact of the areal electron dose rate is investigated. Figure 34 displays three different series recorded on separate windows using an areal electron dose rate of 10 e−/(Å² s), 100 e−/(Å² s), and 1000 e−/(Å² s), respectively. For each setting of the areal electron dose rates, the exposure time and number of spectra were adjusted according to the description in Section 4.2, ensuring an identical accumulated electron dose on each window. Figure 34 displays the oxidation level without any correction for the O₂ gas peak convolution, as the final references for the 10 e−/(Å² s) and 100 e−/(Å² s) series are too divergent, resulting in a failure of the correction according to the discussion above. For the 100 e−/(Å² s) series, the final reference is relatively low compared to the end measurement with gas in the reactor, similar to what was seen for the 80 keV series, and possible due to specimen drift. The correction will therefore lead to starting level lower than the initial reference. For the 10 e−/(Å² s) series, the final reference lies above the oxidation level of the end measurement, which on the time of writing is unexplained. The gas convolution correction will therefore raise the oxidation level, which is unreasonable.

Figure 34 demonstrates a relatively homogeneous level of the initial oxidation of the windows, where the 1000 e−/(Å² s) series lies a bit higher than the rest. In contrast, a considerable variation in the
oxidation rates within the first regime is seen, which seems to be dependent on the value of the areal electron dose rate. Here, a largest areal electron dose rate result in a high oxidation rate within the first regime. For the second regime, the oxidation rate implies to have a different behaviour. Figure 34 reveals that the lowest oxidation rate ($8.52 \times 10^{-7} \text{ (e}^-/\text{Å}^2\text{)}^{-1}$) within the second regime is seen for the 1000 e$^-/(\text{Å}^2\text{s})$ series, whereas the oxidation rate for the 10 e$^-/(\text{Å}^2\text{s})$ series is ($20.6 \times 10^{-7} \text{ (e}^-/\text{Å}^2\text{)}^{-1}$). For the 100 e$^-/(\text{Å}^2\text{s})$ series, the oxidation does not seem to propagate linear, as a more rapid oxidation is observed at the start and then fading off as the oxidation evolves. If, however, the oxidation is fitted by a first order regression, an oxidation rate of ($16.7 \times 10^{-7} \text{ (e}^-/\text{Å}^2\text{)}^{-1}$) is revealed.

Finally, the fitted oxidation rates within the first and second regime from all the experiments have been collected in Table 2, trying to provide an overview over the results. If it has not been clear to the reader so far, it should be stressed that the series illustrated by the blue circles in all figure in fact is the same series, which representing the fixed parameter space. This series therefore works as a reference series compared to the other. Its oxidation rates will therefore also be seen several times within Table 2.

**Table 2: Collection of the oxidation rates for the two regimes for the experiments.**
The table provide to oxidation rates determined from first order regression to the data in the two regime. The oxidation rate is obtained from data without any correction for the gas peak convolution.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Regime 1 [((e$^-$/Å$^2$)$^{-1}$)]</th>
<th>Regime 2 [((e$^-$/Å$^2$)$^{-1}$)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 mbar</td>
<td>$1.52 \times 10^{-6}$</td>
<td>$3.44 \times 10^{-7}$</td>
</tr>
<tr>
<td>100 mbar</td>
<td>$3.44 \times 10^{-6}$</td>
<td>$5.12 \times 10^{-7}$</td>
</tr>
<tr>
<td>500 mbar</td>
<td>$8.37 \times 10^{-6}$</td>
<td>$8.52 \times 10^{-7}$</td>
</tr>
<tr>
<td>1000 mbar</td>
<td>$14.1 \times 10^{-6}$</td>
<td>$12.7 \times 10^{-7}$</td>
</tr>
<tr>
<td>30 $^\circ$C</td>
<td>$10.6 \times 10^{-6}$</td>
<td>$16.2 \times 10^{-7}$</td>
</tr>
<tr>
<td>100 $^\circ$C</td>
<td>$0.70 \times 10^{-6}$</td>
<td>$16.1 \times 10^{-7}$</td>
</tr>
<tr>
<td>500 $^\circ$C</td>
<td>$8.37 \times 10^{-6}$</td>
<td>$8.52 \times 10^{-7}$</td>
</tr>
<tr>
<td>80 keV</td>
<td>$9.88 \times 10^{-6}$</td>
<td>$13.5 \times 10^{-7}$</td>
</tr>
<tr>
<td>300 keV</td>
<td>$8.37 \times 10^{-6}$</td>
<td>$8.52 \times 10^{-7}$</td>
</tr>
<tr>
<td>10 e$^-/(\text{Å}^2\text{s})$</td>
<td>$2.74 \times 10^{-6}$</td>
<td>$20.6 \times 10^{-7}$</td>
</tr>
<tr>
<td>100 e$^-/(\text{Å}^2\text{s})$</td>
<td>$5.53 \times 10^{-6}$</td>
<td>$16.7 \times 10^{-7}$</td>
</tr>
<tr>
<td>1000 e$^-/(\text{Å}^2\text{s})$</td>
<td>$8.37 \times 10^{-6}$</td>
<td>$8.52 \times 10^{-7}$</td>
</tr>
</tbody>
</table>
Table 3: Physical properties of Si$_3$N$_4$ and SiO$_2$. The data is adopted form Fundamentals of semiconductor fabrication [66].

<table>
<thead>
<tr>
<th></th>
<th>Density (g/cm$^3$)</th>
<th>Molar Weight (g/mol)</th>
<th>Molar Volume (cm$^3$/mol)</th>
<th>Molecule Density (molecule/cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si$_3$N$_4$</td>
<td>3.40</td>
<td>140.28</td>
<td>41.26</td>
<td>$1.46 \times 10^{22}$</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>2.21</td>
<td>60.08</td>
<td>27.18</td>
<td>$2.22 \times 10^{22}$</td>
</tr>
</tbody>
</table>

4.6 ESTIMATION OF OXIDE THICKNESS

This section will try to estimate how thick an oxide layer is created during the oxidation process and how much of the original nitride layer that is remaining. To do so, a number of assumption has been made, and is listed here:

- The silicon nitride window material is stoichiometric and thus, the ratio is three silicon to four nitrogen atoms, i.e. Si$_3$N$_4$.
- The amount of Si atoms are conserved in the window material, and are not liberated into the gas phase.
- The Si$_3$N$_4$ is substituted by SiO$_2$.

The initial conditions for the reactor after creation involves an individual window thickness of 15 nm, which consist of a pure amorphous silicon nitride. For the pure Si$_3$N$_4$ windows, the areal molecule density is $4.38 \times 10^{16}$ molecules/cm$^2$, computed from the molecule density (listed in Table 3) times the total thickness of the two windows. The initial areal density of Si atoms in the windows can be calculated from the stoichiometric ratio and the areal molecule density, given as:

$$\text{Si}_{\text{init}} = 3 \cdot 4.38 \times 10^{16} \text{atom/cm}^2 = 1.31 \times 10^{17} \text{atom/cm}^2. \quad (19)$$

Similarly, the initial areal density of N atoms can be calculated as:

$$\text{N}_{\text{init}} = \frac{4}{3} \text{Si}_{\text{init}} = 1.75 \times 10^{17} \text{atom/cm}^2. \quad (20)$$

As the oxidation begins, the Si$_3$N$_4$ is substituted by SiO$_2$ and the nitrogen is liberated into the gas phase. As the oxidation propagates the atomic ration between the oxygen and the nitrogen starts to change. The measured atomic ratio can be expressed as:

$$\frac{O}{N} = \frac{X \cdot 2 \text{Si}_{\text{init}}}{(1-X) \cdot \frac{4}{3} \text{Si}_{\text{init}}}, \quad (21)$$

where $X$ denotes the conversion of the Si atoms. Here, the atomic ratio between the oxygen and nitrogen species are attained from the EELS measurements presented above. Hence, the conversion of Si atoms can be deduce to:

$$X = \frac{\frac{2}{3} \frac{O}{N}}{1 + \frac{2}{3} \frac{O}{N}}. \quad (22)$$
4.6 Estimation of oxide thickness

Figure 35: Estimation of the total thickness of the Si$_3$N$_4$ and SiO$_2$ layers of the nanoreactor windows during oxidation. A The total thickness is depicted as a function of the conversion of Si atoms as Si$_3$N$_4$ is substituted with SiO$_2$. B The total thickness is depicted as a function of the atomic ratio between oxygen and nitrogen as Si$_3$N$_4$ is substituted with SiO$_2$.

In the extreme case, where all Si atoms are converted from Si$_3$N$_4$ to SiO$_2$ (X = 1), the density of Si atoms equate the density of SiO$_2$ (i.e. $n_{Si} = n_{SiO_2}$). This results in a significant change in the total thickness of the windows, where the total window thickness becomes:

$$t_{SiO}(X = 1) = \frac{1.31 \times 10^{17}}{2.22 \times 10^{22}} \text{molecule/cm}^2 = 59 \times 10^{-7} \text{ cm.} \quad (23)$$

This is a doubling in the total window thickness compared to the initial thickness of 30 nm. In general, the total thickness of the remaining Si$_3$N$_4$ layer of the window can be express as a function of the conversion as:

$$t_{Si_3N_4}(X) = \frac{(1 - X) \cdot \frac{1}{3} Si_{init}}{1.46 \times 10^{22} \text{molecule/cm}^3}. \quad (24)$$

Similarly, the total thickness of the SiO$_2$ can be expressed as:

$$t_{SiO_2}(X) = \frac{X \cdot Si_{init}}{2.22 \times 10^{22} \text{molecule/cm}^3}. \quad (25)$$

By combining Equation 22 with Equation 24 and Equation 25, the thickness of oxide layer and the remaining Si$_3$N$_4$ can be calculated.

Figure 35 displays the estimated thickness of the SiO$_2$ and the Si$_3$N$_4$ layer as a function of either the conversion of Si atoms (Figure 35 A) or as the measured atomic ratio (Figure 35 B). For the measurements present above, the minimum value of final references observed was for the 10 mbar series presented in Figure 28 with an atomic ratio of around 0.28. That results in an estimated thickness of the SiO$_2$ layer of 9 nm and a thickness of the remaining Si$_3$N$_4$ layer of 25 nm. For the maximum value of final references observed, an atomic ratio of 0.71 is measured for the 100 °C series, displayed in Figure 32. Such value correspond to an oxide layer of 19 nm, where the remaining Si$_3$N$_4$ has a thickness of 20 nm.
4.7 DISCUSSION

Regarding the question about the integrity of the NR windows, the findings clearly demonstrate that the windows are vulnerable to oxidizing environments while illuminated by the electron beam. Hence, the common assumption that the Si-based windows are chemical inert is rejected. At this point, it is also clear that the electron beam plays an essential role for the process to occur, as the oxidation process only occurs while the electron beam illuminates the specimen.

It would indeed be elegant to provide a fully developed model of the process, however, the process is fairly complex, as illustrated by Figure 36, where many and possible mutually dependent factors are involved, e.g. being both operational and illumination parameters. Due to time, it is not the goal in this thesis to deliver a comprehensive description of the processes, but rather to give hints to how such process may work and how the parameters could influence it. Thus, the goal becomes to determine how the process can be minimized in terms of the investigated parameters, such that future experiments can be conducted without suffering from a lack of window integrity.

To illustrate the complexity of the system, a reconstruction of the model-sketch (Figure 27) is depicted in Figure 36, outlining possible parameters influencing the oxidation process. The influence of the electron beam on the system might be many, but normally three main mechanisms are highlighted, namely [72]:

- knock-on interaction through elastic scattering events, where the incident electrons transfer kinetic energy and momentum to the atoms,
- radiolysis caused by ionization processes through inelastic scattering events, and
- electrostatic charging of the materials induced by the incident electron beam.

Generally, the knock-on cross-section is around 2-3 orders of magnitude lower than the total elastic cross-section. Meanwhile, the inelastic scattering is slightly more dominant for lighter elements than the elastic [72], which speaks for an inelastic interaction as the dominating factor for the oxidation process. As it is shown that a neutral gas is not sufficient to initiate the oxidation, it is obvious to suspect an inelastic electron-gas interaction as the crux of the matter. This interaction can either be stimulated by the incident electrons or by secondary electrons ($e^{-}$) from the windows, generated by the incident electrons. These inelastic electron-gas interactions can induce multiple possible mechanisms, as illustrated by Figure 36, including...
Figure 36: Sketch of possible mechanisms relevant for the oxidation process. In the system sketch, the number of oxygen ($n_O$) and nitrogen species ($n_N$) is measured by the electron probe, trying to describe the thickness of the oxide ($t_{oxide}$) and nitride layer ($t_{nitride}$). In the experiment, parameters that are varied include the pressure ($P$), the temperature ($T$), the areal electron dose rate ($r_{areal}$) and the primary electron energy ($E_0$). The incident electrons can induce an electric field ($E_{field}$) in the window materials and/or generate secondary electrons ($e^-$). Concurrently, the electron-gas interactions, either from the incident electrons or the secondary electrons, are occurring, resulting in possible ionization or radiolysis processes, which can be expressed by a total inelastic interaction cross-section ($\sigma_{inel}$). Simultaneously, parameters such as the gas flow ($v$), the window resistivity ($\rho_{SiO_2}$ and $\rho_{SiN_x}$) and the gas density influence, when varying the operational parameters. Eventually, all of these mechanisms and parameters will influence the oxidation process, described by the flux of oxygen ($\Phi_O$) into the window material and the flux of nitrogen ($\Phi_N$) out of the window material.

Ionization, radiolysis, creations of radicals and more, and are collectively expressed by a total inelastic cross-section ($\sigma_{inel}$). Furthermore, the incident electrons can induce an electric field within the windows. Especially for insulating materials (as the windows), holes in the valence band, generated by emission of secondary electrons, cannot be neutralized immediately, resulting in positive charge trapped within the illuminated area [72]. Such generated fields might help attract charged oxygen species toward the surface of the windows. Here, both the strength of the electrical field and the yield of secondary electrons will depend on the resistivity of windows ($\rho_{SiN_x}$ and $\rho_{SiO_2}$), which might change as the thickness of the oxide layer ($t_{oxide}$) grows.
When consulting the operational conditions, the findings overall indicate that a low pressure and a high temperature is needed to limit the oxidation process. This is demonstrated by the oxidation rates listed in Table 2. Here, the oxidation rates within both regimes demonstrate a nearly linear dependency on the pressure. That is expected as an increasing of the pressure eventually will lead to a large number of oxygen species in the reactor, which can react with the windows. Besides, a larger density of molecules also increases the chances of inelastic interactions between electrons and gas molecules.

As for the temperature, the picture is not that obvious. For the low temperature series, a similar oxidation rate is observed, which is twice as large as for the high temperature series. When it comes to the oxidation rates within the first regime the tendency is more vague, as the 100 °C series demonstrates an almost non existing oxidation rate. However, as it was pointed out earlier, it would be recommended to remeasure this particular series, as the behaviour of the series seems to deviate from the rest of the series and the prevalent understanding. If the 100 °C series is temporarily sent to the corner, the tendency appears more clear. Then the oxidation rates for both the first and second regimes indicate that a more rapid oxidation is present at low temperatures (30 °C) than for higher temperatures (500 °C). This tendency, however, cuts against what was expected, as it was anticipated that a higher temperature would increase the oxidation rate, since more energetic oxygen species are more likely to overcome the activation barrier related with the oxidation.

Another considerable effect of the temperature variation is that a thinning of the gas will occur, cf. the ideal gas law. An elevation from 100 °C to 500 °C will result in a halving of the gas density, whereas an increase from 30 °C to 100 °C only will lead to a reduction of 20 %. If the amount of oxygen species in fact is the crux of the matter and the temperature is irrelevant, then the percent-wise reduction of gas density will be reflected in the oxidation rates. For the oxidation rates in the second regime, a reduction less than 1 % is observed when going form 30 °C to 100 °C. However, a reduction of around 53 % is seen when heating from 100 °C (1.61 × 10^{-7} \text{ e}^-/\text{Å}^2) to 500 °C ((8.52 × 10^{-7} \text{ e}^-/\text{Å}^2)). The discussion can further be addressed by comparing the measurements acquired at 500 mbar and 100 °C with the measurements acquired at 1000 mbar and 500 °C. See also Figure 52 in Figure A for direct comparison. For these two series, the gas density is identical and thus, the oxidation rate should be too, if the temperature in fact is irrelevant. This, however, is not the case, meaning that the temperature must stimulate other effects, which must account for the more rapid oxidation at lower temperatures. That could likely be the resistivity of the window materials, as it is seen for SiC-films in other MEMS devices [26], which will affect the
yield of secondary electrons and the strength of a possible electric field in the specimen.

Finally, variation of both the pressure and the temperature will change the flow rate of molecules ($v$) through the reactor zone. As the flow rate of the reactor is defined by the pressure gradient across the reactor, an elevation of the pressure will increase the flow rate. For an elevation of the temperature, the gas density will decrease, but as the inlet flow rate is constant, the flow rate through the warm reactor zone will increase. The highest gas flow used here are comparable to Vendelbo et al. [73] and Vendelbo et al. [42], which suggested that the residence time of the molecules are comparable with the thermal equilibration time of the hot zone. Hence, if any, only limited effect of the gas flow is expected.

For the illumination conditions, the findings demonstrate that a high primary electron energy is preferable to minimize the oxidation. In general, a lower primary electron energy will enhance the electron interaction with the specimen-gas system [6]. As an example, the total ionization cross-section for O$_2$, calculated by the relativistic binary-encounter-Bethe model [57, 58], increases from a value of $\sigma_{\text{RBEB}}(\text{O}_2, 300\text{ keV}) = 1.38 \times 10^{-2} \text{ Å}^2$ to $\sigma_{\text{RBEB}}(\text{O}_2, 80\text{ keV}) = 2.97 \times 10^{-2} \text{ Å}^2$ when lowering the primary energy from 300 keV to 80 keV. Since the oxidation is driven by the electron beam, it is anticipated that a higher interaction between the electrons and the specimen-gas system will increase the oxidation. This is confirmed by the oxidation rates listed in Table 2, showing higher oxidation rates for both regimes at 80 keV. However, an ionization of the gas by the incident electrons cannot describe the variation in oxidation rate alone, as the total ionization cross-section is reduced by 53%, going from 80 keV to 300 keV. In comparison, the oxidation rate in regime 1 is reduced by 66%, where the reduction for regime 2 only is 37%.

The behaviour of the areal electron dose rate is more tricky to outline. Normally, beam induced effects are strongly proportional to the electron dose rate [18, 24, 26, 29, 74, 75], as it was seen in Chapter 3 and will be shown in Chapter 6. That is also the case for the oxidation rates within the first regime, where the lowest oxidation rate is seen at $10 \text{ e}^-/(\text{Å}^2\text{ s})$ and the highest oxidation rate at $1000 \text{ e}^-/(\text{Å}^2\text{ s})$, as demonstrated in Table 2. This indicates that the inelastic scattering is determined by areal electron dose rate. However, for the oxidation rates in the second regime the picture looks different, as the highest oxidation rate belongs to the $10 \text{ e}^-/(\text{Å}^2\text{ s})$ series and the lowest oxidation rate is owned by the $1000 \text{ e}^-/(\text{Å}^2\text{ s})$ series. Moreover, the trend of the oxidation, especially for the $100 \text{ e}^-/(\text{Å}^2\text{ s})$ series, does not really seem to be linear in its regression, but rather second order. That might imply that the oxidation slowly decrease as the oxidation evolves. These observations imply a change in the dominating mech-
anism. It could be speculated that the bulk diffusion across the initial oxide layer is dependent on the areal electron dose rate and becomes faster with a lower areal electron dose rates because the induced electric field becomes weaker and retards diffusion less (see Figure 36).

If the oxidation is considered in terms of the exposure time instead of the accumulated electron dose, it is beneficial to operated the microscope with a low areal electron dose rate. For the $1000 \text{e}^-/(\text{Å}^2 \text{s})$ series, each spectrum took 10 s to record, whereas the same time for the $10 \text{e}^-/(\text{Å}^2 \text{s})$ were 1000 s or approximately 17 min. Thus, a low areal electron dose rate gives a larger time span to study the specimen with lowest possible oxidation occurring. However, it comes with the cost of a reduced image signal.

4.8 Conclusion

It has been demonstrated that the common assumption, implying that the silicon-based windows of the NR are chemically inert, is dismissed for oxidizing environment while illuminated by the electron beam. The findings indicated that both operational conditions, being pressure and temperature, and illuminated conditions, meaning the primary energy and the areal electron dose rate, all are vital for minimizing the oxidation of the windows. To minimize the oxidation of the windows, it is recommended to maintain a low pressure and areal electron dose rate, simultaneously with a high temperature and primary electron energy. A first draft of a model is delivered, providing hints to possible mechanisms and processes which might stimulate the oxidation. Further studies are necessary to finish the model and provide a complete description of the oxidation process.
In the previous chapters, strengths as well as the limitations of the NR system has been addressed. Here, the true power of the NR system is demonstrated while studying the structure and functionality relationship for Pt NPs during catalytic oxidation of CO.

This chapter will question how the catalyst structure and activity is commonly related. The chapter will deliver a comparison between the global integral activity, determined by MS, and a local probing of the local environment the catalyst is position in, estimated by EELS. Finally, the nano-structure of the catalyst is related to the two methods. The work presented in this chapter has been conducted in close cooperation with Christian F. Elkjær from Haldor Topsoe A/S and with guidance from Søren B. Vendelbo from Technical Institute of Denmark. The work is in preparation for publication and is listed as paper A in the publication list.
5.1 INTRODUCTION

A fundamental question within the field of catalysis research is how the structure of the catalyst relates to its functionality. This has for long been the holy grail in catalysis and has been studies in detail in a vast range of different in situ and operando techniques [27, 42, 76–82]. These techniques include a vast number of photon-based methods, which average over a large number of catalytic NPs, and (S)TEM, where a minor ensemble of NPs are examined. The determined NPs structure are regularly related to activity measurements obtained by means of MS of the gas exiting the reactor bed. However, such operando techniques may in the current state-of-the-art be misleading because [42]:

• the gas composition vary in space across the catalytic reactor
• the NPs dynamically adjust their structure and function to the local environment

Using a global integral of the NPs structure and/or their functionality might result in misinterpretation and misleading within the commonly accepted understanding of the catalytic structure-activity relationship.

Within the recent years, it has been demonstrated how EELS can be utilized to determine the composition of the gaseous environment during catalytic activation [81, 82]. This provides a local probing of the local environment around the catalytic NPs. By employing the local environmental probing method [81, 82] to the novel NR system, it becomes possible to provide a direct comparison between the global integral (MS) and the local probing of the gas composition during catalytic reactions. Here, a well-studied model system [83], the catalytic oxidation of CO to CO₂ over Pt NP, is used to showcase the comparison of a global and local measurement reaction conversion and how these relates to the structure of NP at the atomic scale.

5.2 METHOD

The experiment was performed while operating the FEI Titan 80-300 ETEM microscope with a primary electron energy of 80 keV and an total electron dose rate around 1 nA. Before the experiments, the Cs-corrector was tuned to a Cs-coefficient between −5 µm to −20 µm, resulting in an image resolution of 1.0 Å. Follow to the tuning of the Cs-corrector, the post-column GIF system was tuned in vacuum and without any specimen present in the field-of-view.

Furthermore, a low areal electron dose rate below 20 e⁻/Å²s was applied to minimize beam induced effects. Additional electron dose rates of 5 e⁻/Å²s, 40 e⁻/Å²s and 80 e⁻/Å²s were tried out, re-
revealing no influence on the EEL spectra, whereas the aspect of particle sintering was negatively affected by an areal electron dose rates higher than $20 \text{ e}^-/\text{Å}^2 \text{s}$. Both the areal and total electron dose rate were controlled based on measurements on the pre-GIF CCD camera without any specimen in the field-of-view. Here, the CCD camera was calibrated, as earlier described, by measuring the current output from the drift-tube while trapping the incoming electron beam in the drift-tube, which led to an conversion factor of $7.66 \text{ counts/e}^-\text{ for } 80\text{ keV}$.

A Dimes NR was loaded with Pt NRs according to the procedure described in Section 2.2.4, using a salt solution of tetraammineplatinum(II)nitrate in water as the precursor. The NR was mounted in the Titan microscope, where the calcination and reduction were performed prior to the experiment. The experiment was initialized by introducing a mixture of O$_2$ and a premixed CO: Ar = (50 : 50) gas to the reactor inlet, controlled by thermal mass flow meters. The flow rates were 4 mL/min for O$_2$ and 2 mL/min for CO: Ar, corresponding to a gas composition of CO: Ar : O$_2$ = 1 : 1 : 4 of the inlet gas. The gases were mixed at a pressure of 2 bar. Before entering the NR, the mixed gas was passed through an active carbon filter to remove Ni-carbonyls. The outlet of the reactor was connected directly to the mass spectrometer and pumped by a dedicated TMP to a pressure of $10^{-5}$ mbar. That results in a pressure of 1 bar inside the reactor zone of the reactor due to the symmetry of the NR [23, 39, 42]. The mass spectrometer continuously monitored the ion current at 28 u, 32 u, 40 u and 44 u, which were associated by the signals from CO, O$_2$, Ar, and CO$_2$. The four ion currents were sampled with a dwell time per mass of 0.1 s.

The experiment was executed by elevating the temperature step-wise from 100 °C, where zero conversion was assumed, to 550 °C, assuming that full conversion was achieved. At each step in temperature, TEM images were recorded to document the particle shape, and EEL spectra to determine the ensemble conversion. Figure 37 demonstrates the experimental procedure applied for the temperature steps of 200 °C, 300 °C and 350 °C, however, the producer was repeated for all other temperature steps as well. TEM images were recorded with the pre-GIF CCD camera at three different magnifications, corresponding to a pixel size of 0.79 Å, 1.56 Å and 5.13 Å, which were calibrated prior to the experiment using a Mag*T*Cal standard grid. Here, the first two magnifications are used to document the particle shapes, whereas the latter was used to capture the entire electron illumination on the specimen. TEM images at all three magnifications were recorded prior to the EELS acquisitions, as illustrated in Figure 37. Right after the EELS acquisitions, a TEM image of the entire electron beam was recorded to evaluate the specimen drift.
Figure 37: Experimental procedure for the examination of the Pt nanoparticles during catalytic oxidation of CO to CO$_2$. The temperature was stepwise elevated from 100 $^\circ$C to 550 $^\circ$C at 1 bar constant pressure of CO : Ar : O$_2$ = (1 : 1 : 4) in the reactor zone. At each step, TEM images at 16.5 kx, 56 kx and 115 kx magnification, corresponding to a CCD pixel size of 0.79 Å, 1.56 Å and 5.13 Å, were acquired together with EELS. Here, the schematic only shows the experimental procedure for temperature step 200 $^\circ$C, 300 $^\circ$C and 350 $^\circ$C, but the procedure was applied to each temperate steps from 100 $^\circ$C to 550 $^\circ$C.

All EEL spectra were recorded by the post-column GIF-camera while operating the TEM projector system in diffraction mode, using a 2 mm entrance aperture and an energy dispersion of 0.2 eV/pixel. As a result, a FWHM of 0.8 eV was established for the ZLP. The CL spectra of the C-K edge were recorded as a series of 80 spectra, where each of the spectra was acquired as a running sum of the 20 individual recordings with an exposure time around 0.14 s. Each spectra in the series was shifted 0.2 eV with respect to the previous in order to compensate for dark current noise. After the recordings, the 80 spectra were aligned and summed to a final spectrum. This procedure was adopted to gain a sufficient SNR of the C-K ionization edge. Consequently, the final recording time was estimated to around 5 min, including readout delay. In practice, each spectra holds an internal energy dispersion calibration using the N-K ionization edge from the window material, located at 401.6 eV, and the O-K ionization edge from the gas, located at 532 eV. However, additional recordings were also performed on a BN-specimen used to calibrate the energy dispersion.

5.3 DATA QUANTIFICATION

Prior to the experiments, all data acquisitions was synchronized to the time stamp of the main microscope computer. Doing so, the time stamp in each TEM image or EEL spectrum was used as the time reference within the data synchronization. The data treatments were performed using Python 3.0, where the Hyperspy module [84] was utilized to handle the TEM images and EEL spectra.
5.3.1 Mass Spectrometry Quantification

Figure 38 A illustrates a typical MS spectrum for the experiment, demonstrating how the signal of CO and O₂ decreases as the temperature is elevated from 100 °C to 550 °C, simultaneously with the CO₂ signal increases. As the temperature increases during the experiment, the total gas flow rate through the NR will change to lower rates. In addition, the total pressure remains constant at all temperatures and flow rates, due to the design of the NR system. Thus, the following procedure is applied to quantify the reactor conversion from the exit gas components.

The global reactor conversion is estimated based on analysis of MS. Here, the CO conversion (X_{CO}) is calculated in terms of the CO ion current signal. In order to compare the global reactor conversion to the local environmental conversion, the MS signals are evaluated within the time spans where the EEL spectra were recorded, i.e. approximately 5 min. Here, an average value of each of the ion current signals (28 u, 32 u, 40 u and 44 u, corresponding to CO, O₂, Ar, and CO₂) are calculated for all of the temperature steps. To quantify the CO conversion during the experiment, the ion currents were normalized based on the Ar signal, i.e. the ion current at 40 u (i_{m40}). This action was performed to compensate for overall drift of the MS sensitivity and the decrease in the overall flow rate upon temperature elevation, due to the temperature dependent flow restriction of the NR micro-channel [42]. Besides, a fraction of the CO₂ will be cracked when analyzed in the mass spectrometer, which results in an increase of the ion currents at 28 u (i_{m28}), corresponding to 11.4% of the ion current signal at 44 u (i_{m28}) [44]. That is compensated for
by a dynamic background subtraction based on the ion current signal at 44 u.

\[
ic_{\text{CO, norm}}(T) = \frac{ic_{\text{m}28}(T)}{ic_{\text{m}40}(T)} - 0.114 \frac{ic_{\text{m}44}(T)}{ic_{\text{m}40}(T)}
\] (26)

The CO conversion was determined as the change in the normalized CO signal compared to the initial CO signal at 100 °C (\(ic_{\text{CO, init}}\)), where it was assumed that no conversion occurred.

\[
X_{\text{CO}} = \frac{ic_{\text{CO, init}} - ic_{\text{CO, norm}}(T)}{ic_{\text{CO, init}}}
\] (27)

5.3.2 Electron Energy-Loss Spectroscopy Quantification

The local environmental conversion is estimated by analysis based on EELS. The analysis builds on the chemical shift of the C-K ionization edge between CO (286.4 eV) and CO\(_2\) (289.7 eV) [81, 82] as illustrated by the background subtracted EEL spectra in Figure 38. To extract the C-K peak, a usual inverse power law is fitted previous to the C-K edge and extrapolated beyond the edge, where it is subtracted. From the background subtracted spectra, the amount of CO and CO\(_2\) are determined from the intensity of the two peaks, defined by the interval from 286 eV to 287 eV for CO and 289.5 eV to 290.5 eV for CO\(_2\).

When the temperature is raised during the experiment, the density of gas molecules in the reactor zone is reduced. To compensate for this, a normalization of the peak heights (\(I_{\text{CO, norm}}(T), T\) is temperature in K) is calculated according to

\[
I_{\text{CO, norm}}(T) = \frac{I_{\text{CO}}(T)}{I_{\text{CO, init}}} \cdot \frac{T}{372.15K}
\] (28)

where \(I_{\text{CO, init}}\) refers to the initial peak height at a reference temperature of 100 °C, where it is assumed that no conversion is taking place. The second fraction corrects for the peak reduction due to the temperature dependent decrease in gas density.

When the conversion starts to occur, the total amount of gas molecules is reduced due to the stoichiometry of the reaction, and because the NR is operated at constant pressure, the partial pressure of the residual gas will eventually increase. Therefore, a total equivalent pressure \(P(X)\) is introduced, expressing the partial pressure composition as a function of the conversion \(X\) as if the experiment was conducted in batch mode.

\[
P(X) = P_{\text{CO}}(X) + P_{\text{O}_2}(X) + P_{\text{CO}_2}(X) + P_{\text{Ar}}(X)
\] (29)
P(X) can be expressed in terms of the initial conditions, using a constant reactor pressure of 1000 mbar and an initial gas composition of CO:Ar:O₂ = 1:1:4, it results in

\[ P(X) = 250 \text{ mbar} \cdot (1 - X) + 500 \text{ mbar} \cdot (1 - 0.5X) + 250 \text{ mbar} \cdot X + 250 \text{ mbar} \]

\[ = 1000 \text{ mbar} \cdot \left(1 - \frac{1}{12}X\right) \]

The ensemble conversion can now be calculated, applying \( P(X) \) to compensate for the changes in the gas composition.

\[ X(T) = 1 - I_{CO, norm}(T) \cdot \left(\frac{P(X)}{1000 \text{ mbar}}\right) \]

If \( P(X) \) is expressed in terms of the initial conditions as in Equation 31, \( X(T) \) is finally described by

\[ X(T) = \frac{1 - I_{CO, norm}(T)}{1 + \frac{1}{12} \cdot I_{CO, norm}(T)} \]

5.4 Pt Coverage of the Nanoreactor Windows

Figure 39 displays an overview of all 41 windows of the Dimes NR upon loading, showing the coverage of Pt NPs on the individual windows. From the overview, it is clear that some windows are more densely loaded than others.

To give a estimate of the variation in the Pt coverage of the windows, a segmentation procedure was adopted as illustrated by Figure 40. The segmentation was performed by ImageJ [85], where a RenyiEntropy threshold was applied (shown in Figure 40 B). By guidance from the original TEM image, the window area was outlined as indicated by the yellow circle in Figure 40 A and B. The Pt coverage was calculated from within the marked window area. This approach was adopted as to avoid unwanted contributions from the diffraction contrast of the window edges.

Figure 40 C displays the estimated Pt coverage for each of the windows, as well as the window area expressed in terms of the window diameter. The window numbers plotted in Figure 40 corresponds to the image depicted in Figure 39. The analysis reveals a mean Pt coverage of 7.8 %, which equates a mean projected area of 2.2 \( \mu \)m² per window. From Figure 40 and Figure 39 a threshold is estimated, defining Pt coverage above 10 % (or a projected area of 2.8 \( \mu \)m²) as a dense coverage window and Pt coverage below as sparse loaded windows. These dense loaded windows are highlighted in Figure 39 by a superimposed white H (for High).
Figure 39: Overview of the Pt NPs coverage on the nanoreactor windows. The electron transparent windows are displayed, illustrating the coverage of Pt NPs at each separate windows. The high density coverage window is marked by a super-imposed white H (High) and is defined by a coverage over 10% of the window area. Each image measures 6.5 µm × 6.5 µm.

5.5 Local versus Global Activity

Figure 41 displays the local conversion (black points) measured by EELS at different positions in the NR and the global conversion (blue points) measured with MS of the exit gas versus the temperature of the reactor zone. Figure 41 A-B represent the measurements at two separated windows with a sparse window coverage of the Pt NPs of 7.8% and 3.6%, respectively. Here, Figure 41 A is acquired from a window positioned at the reactor inlet, whereas Figure 41 B is obtained from a window located at the outlet of the reactor zone. For both Figure 41 A and Figure 41 B, the global measurement shows that the CO conversion initiates around 350 °C and that the lift-off happens around 410 °C, where the global conversion rise dramatically from
Figure 40: Estimation of the reactor coverage of Pt NPs. A displays the original TEM images, where the window area is defined by the superimposed yellow circle. B displays the segmentation of the TEM image, from which the coverage of Pt NPs are determined within the area restricted by the superimposed yellow circle. C depicted the estimated coverage for all the 41 electron transparent windows (shown in Figure 39), as well as the measured window area, expressed by diameter. The dashed line illustrates the threshold for the dense and sparse coverage, defined as above or below 10%, respectively. The average coverage is 7.8%, which equates a projected area of 2.2 µm².

0.11 at 400 °C to 0.64 at 410 °C for Figure 41 A, and similar from 0.17 to 0.66 for Figure 41 B. Meanwhile, the local conversion measured at the inlet of the reactor is only increased from 0.03 to 0.22, whereas the local conversion measured at the outlet rises form 0.19 to 0.77. As the temperature is further increased, the global conversion remains increasing steadily until full conversion is obtained at around 525 °C. During this time, the local conversion at the inlet remains lower than the global, while increasing steadily until it reaches full conversion at around 550 °C. Concurrently to this, the local conversion measured at the outlet stays above the global until approximately 475 °C, from where they maintain similar values for the rest of the experiment.

This indicates that a gradient of the CO concentration along the flow direction in the NR is present. This is in agreement with simulation previous reported for the same NR design under similar opera-
Figure 41: Comparison of global and local CO conversion at different position in the nanoreactor. The displays show the global (blue) and the local (black) conversion as a function of the temperature at different location in the reactor. A Position at the reactor inlet with a sparse window coverage (7.8\%). Shows a lower local conversion than the global. B Position at the reactor outlet with a sparse window coverage (3.6\%). Shows an identical local and global conversion. C Position at the reactor inlet with a dense window coverage (31.5\%). Shows a local conversion that rise to 1 at lift-off, i.e. higher than the global conversion. D Position at the reactor outlet with a dense window coverage (16.3\%). Shows a local conversion that rises to 1 at lift-off, i.e. higher than the global conversion.

This underlines the importance of local activity measurements, in particular when linking structural changes of the catalyst to its activity. Here, the findings demonstrate how the catalyst NPs experience considerably different environments depending on the location in the reactor, which might vary vastly from what is integrally measured by MS of the exit gas. For instance, a low Pt coverage area at the outlet of the reactor might be fairly well represented by a global measurement of the conversion by MS (Figure 41B), whereas a similar window located at the inlet will be incorrectly represented by the global conversion (Figure 41A).

In contrast, high Pt coverage areas demonstrate an entirely different behavior. Figure 41 C-D displays the local and global measured conversion for two dense coverage area with a Pt coverage of 31.5\% and 16.3\%, respectively. Here, Figure 41 C is acquired from an area
placed at the inlet of the reactor and Figure 41 D from an outlet location. At these dense coverage areas, the local and global conversion go together up to around 400°C, from whence the local conversion rises directly to 1.0 (full conversion) for temperatures above the lift-off, which is notably higher than the simultaneously measured global conversion. This is an exclusively local behavior, which is directly linked to the high density of Pt in the area, since this behavior is unobserved on neighboring windows with a low Pt coverage. At these dense Pt coverage areas the behavior is identical for the inlet and outlet, however, at the outlet the local conversion appears to surpass the global already at 380°C (Figure 41 D), even-though the difference is relatively small compared to after lift-off. Nevertheless, high Pt density areas facilitate a similar local environment independent of the location in the reactor, which is purely described by the global conversion.

5.5.1 Bistability

Under a specific combination of the reactor dimensions and flow conditions a reactor might be bistable within a particular temperature interval for a self-poisoning reaction, such as CO oxidation [42, 86–88]. A bistable reactor can obtain a low conversion branch or a high conversion branch depending on the direction the bistable temperature regime is approached. When the regime is approached from lower temperatures (low conversion) the reactor will obtain the low conversion branch, whereas the high conversion branch is achieved when approaching the bistable temperature regime from higher temperatures, i.e. coming from a high conversion.

Figure 42 displays the local and global conversion versus the temperature while approaching the bistable regime, first from the low conversion regime (ramping from 100°C to 500°C), and then from the high conversion regime (ramping from 500°C to 100°C). Figure 42 A represent a sparse Pt density area with a coverage of 2.7% located at the outlet of the reactor. The global measured conversion is initiated at around 350°C and the lift-off occurs between 400°C and 430°C, where the global conversion rises from 0.11 to 0.71. From here, the global conversion increases gradually until it reaches 1.0 (full conversion) at 500°C. Simultaneously with this, the local measured conversion demonstrates exactly identical behavior as the global. That is in consistency with the findings in Figure 41 B, which were acquired at similar Pt coverages and location.

As the temperature is ramped down, the global conversion gradually decreases, following the same curve as under the upward ramping from 430°C. However, the gradual decrease of the conversion continues pass 430°C as it enters the high conversion branch, until it reach 370°C where the global conversion drops from 0.51 to 0.01
**Figure 42:** Comparison of global and local CO conversion within a bistable temperature regime. The displays show the global (blue) and the local (black) CO conversion along a temperature hysteresis loop, ramping from 100 °C to 500 °C to 100 °C.

**A** Position at the reactor outlet with a sparse window coverage (2.7%). Shows an identical local and global conversion along the hysteresis loop. **B** Position at the reactor outlet with a dense window coverage (16.3%). Shows a considerably higher local conversion than global along the hysteresis loop.

(zero conversion) at 350 °C. Here, the global conversion stays at zero conversion for the remaining part of the temperature ramp, i.e. until 100 °C. Concurrently, the local conversion goes together with the global until 430 °C, from where the local conversion starts to decrease faster than the global, but still in a gradual manner till it reaches a level around 0.2 at 350 °C, where it stays with minor fluctuation for the rest of the experiment. In general, the global and local measured conversion seems in tune with each other on a sparse coverage area positioned at the reactor outlet. That is in line with the observation in Figure 41 B.

Figure 42 B represent a dense Pt density area with a coverage of 16.3 %, which is positioned at the outlet of reactor. At this coverage, the global measured conversion demonstrates identical behavior as the sparse coverage area shown in Figure 42 A. In contrast, the local measured conversion only follows with the global until lift-off at 420 °C, from where it goes directly to full conversion. Here it stays until 500 °C where it drops slightly to a conversion around 0.9. On the down ramp, the local conversion stays between 0.88 and 1.0 until 340 °C where it drops directly to 0.16, before it saturates at 0.06.

This findings suggest that the high density areas basically have two modes only: either zero conversion or full conversion. Together with the bistability effect, it demonstrates that a local environmental conversion twice the size of the global conversion is achievable for high density areas.
5.6 STRUCTURE DYNAMICS

The findings above certainly illustrate how the local density of catalytic materials influence on the local measured conversion. How the local coverage influences on the NP morphology is elucidated in Figure 43.

Figure 43 A visualizes the coverage on a sparse density window positioned at the outlet of the reactor and is the host for the measurements presented in Figure 42 A. The image series demonstrates how the morphology of the Pt NPs is restructuring while elevating the temperature from 370 °C to 500 °C followed by cooling to 370 °C. The temperature is denoted in the upper corner in each image. Three of the present particles have got their shapes outlined to emphasize the refacetting of the particles. Upon heating from 370 °C to 430 °C the Pt NPs obtain a more spherical morphology, whereas at 500 °C the particles transform into a more faceted morphology. As the temperature is cooled back to 370 °C the particles returns to a similar spherical structure.

In Figure 43 B, similar demonstration of the particle restructuring is presented for a dense coverage area positioned at the outlet of the reactor. This window is the origin of the activity measurement presented in Figure 42 B. The image series in Figure 43 B visualizes the Pt NPs while ramping the temperature from 380 °C to 500 °C and back to 380 °C. Similarly as in Figure 43 A, the particles obtain a more spherical morphology at the low temperature (380 °C). However, already
at 420 °C the particle starts to transform toward a more faceted morphology, which only gets more distinct as the temperature is raised to 500 °C. The most faceted morphology, however, is obtained as the temperature is cooled down to 380 °C.

The observations reveal that the Pt NPs assume a more spherical morphology in the beginning at lower temperatures, whereas a more faceted shape is associated with higher temperatures. That is consistent with previous report [42, 89]. Moreover, the dense density of Pt seems to give preference to a more faceted morphology. That is expressed as the refacetting of the particles occurs at lower temperature than for the sparse coverage area. Finally, the dense density area allows the particles to remain in the faceted state upon cooling, where the particles are able to stay faceted at temperatures lower than what is possible during the temperature elevation. Conclusively, this implies that the local density of Pt indeed influences the structural behavior of the Pt NPs.

5.6.1 Morphology Factor

To provide a quantitative description of the restructuring of the particles, a particle morphology factor (denoted \( \alpha \)) is defined. The factor is based on the variation between the projected area between the individual particle and a fitted elliptical shape with identical area and center of mass. The procedure is illustrated in Figure 44.

Figure 44 A displays a TEM image visualizing an ensemble of Pt NPs during the oxidation of CO at 380 °C. The structural outline of the NPs can be determined by segmentation of the image and was performed with ImageJ [85]. Prior to the segmentation, the TEM images were filtered by a median filter using a radius of 2 pixel. Each NP was individually selected to create a local threshold for the individual NP using ImageJ’s default settings. The local thresholds and the median
filter helped to deliver a sharper outline of the NPs. The outlines of the Pt NPs after the segmentation is demonstrated in Figure 44 B. Following to this, the segmented NPs were fitted to an elliptical shape with an identical area and center of mass as for the original particle. The outlines of such elliptical particles are illustrated in Figure 44 C.

If the two outlines (the real and the elliptical) are overlayed each other, the areas enclosed by the outlines demonstrates the variation in the projected area between a perfect elliptical particle and the real particle shape. The result of such procedure is demonstrated in Figure 44 D. The philosophy here is that a rounded particle will expand a similar projected area as for the elliptical fitted area, and thus, the variation between the two will approach zero. The more faceted the particle becomes, the larger the variation between the projected area will be. If the variation in the projected area is denoted \( A_i(T) \) as a function of the temperature (T), where \( i \) denoted the index of NPs in the each individual TEM image, then the morphology factor of particle \( i \) is defined as:

\[
\alpha = \frac{A_i(T)}{A_i(100^\circ C)}
\]  

(34)

Here, \( A_i(100^\circ C) \) denotes the initial shape of the particle at 100 \(^\circ\)C in the beginning of the experiment. The morphology factor thus describes the structural change of the particle compared to its initial structure at the beginning of the experiment. By this definition, an increasing value of \( \alpha \) indicates that the particle moves toward a more faceted structure, whereas decreasing \( \alpha \)-value suggests that the particle turns toward a more rounded structure.

It should be mention that the analysis has excluded particles smaller than 25 nm \(^2\) and particles that exceed the edge of the TEM images. The reason for this is that the structural changes is less pronounced for smaller NPs and also, the outline is more difficult to determine due to a low contrast difference.

To elucidate on the structural change of an ensemble of NPs, a mean value of all the particle’s morphology factors was calculated. Regarding the TEM image series shown in Figure 43, the mean morphology factor is denoted in the lower right corner. For the sparse coverage window presented in Figure 43 A, the Pt NPs reveal a mean morphology between 0.93 and 1.01 for the temperature interval of 370 \(^\circ\)C to 430 \(^\circ\)C. Upon heating to 500 \(^\circ\)C the mean morphology factor increases to 1.20, which indicates that the particles turns toward a more faceted state. After cooling to 370 \(^\circ\)C, the factor returns a similar value (0.95) as before heating. For the dense coverage window (Figure 43 B), the morphology factor starts with a value of 0.89 at 380 \(^\circ\)C, from where it keeps increasing to 1.12 at 500 \(^\circ\)C, before ending at a final value of 1.67 at 380 \(^\circ\)C. The morphology factor underlines the observations presented above, revealing that the dense density of Pt favors a more faceted particle shape compared to the low density areas.
It should be stressed that the $\alpha$-value cannot directly be compared across different experiment series as the morphology factor is based on the initial shape of the NPs at 100 °C. Hence, it cannot be concluded that the NPs in Figure 43 A have a more facetted shape at 500 °C than for Figure 43 B, just because Figure 43 A has the highest $\alpha$-value.

### 5.7 Structure and Activity Relationship

In the introduction it was questioned if the global integral measurements of the NPs shape dynamics and/or their activity in fact could be misleading when addressing the structure and functionality relationship for catalytic NPs. As it is demonstrated, both the local structure and the local conversion vary vastly depending on the position in the reactor and the local density of the catalytic materials. Thus, it must be argued that local observed structures should be linked to local measured activity from the same area, as to prevent misinterpretation.

To elucidate this, Figure 45 depicts the local measured conversion as a function of the global, where the color of each point represent the mean morphology factor from the very same area, ranging from black ($\alpha = 0.79$) to bright green ($\alpha = 1.67$). This means that a mean spherical morphology will appear as dark green/black within Figure 45, whereas more faceted particle morphologies are presented as light green, which are indicated by the red square and circle next to the scale bar.

For an ideal case, it would be expected to see a linear relation between the local measured conversion and the global. This, however, is far from the case. Figure 45 demonstrates how the local conversion can take values spanning from half the global to more than double of the global, depending on the location in the reactor and the local coverage of Pt. Here, a local conversion much lower than the global is associated with a sparse coverage area positioned at the reactor inlet (see Appendix B). In addition, local conversions considerably higher than the global can be associated to dense density areas independent on the location (see Appendix B).

Moreover, Figure 45 demonstrates that particles with a faceted structure ($\alpha > 1$, green to bright green) are mainly located toward the upper right corner, determined by a high conversion. Linking the structure to the global measured conversion reveals that the faceted particles lie within a relatively broad interval, ranking from around 0.4 to 1.0, which also holds a similar number of more rounded particles ($\alpha \leq 1$, dark green to black). In contrast, the interval is much narrower if the structure is linked to the local measured conversion. Here, a sharp threshold is observed at 0.85, corresponding to a local CO partial pressure of 25 mbar, where above all the faceted particles are located. Meanwhile, almost no round particles ($\alpha \leq 1$, dark
5.8 discussion

Previously, it has been implied by steady state simulations that a decreasing CO gradient is present along the flow direction of a nanoreactor at high conversion during catalytic oxidation \[42\]. Such gradients are not detectable with MS as it provides a global integral of the entire reactor system, and hence no direct proof of the gradient has been submitted, until now.

By use of a local TEM EELS probe it becomes possible to determine the local environmental composition along the reactor, showing a significant variation between the local and global measurements depending on the position in the reactor and the local density of Pt. Furthermore, the local probing allows to precisely correlate local morpholog-
ical changes of the Pt NPs with the local environment in which they are positioned.

In particular, the findings demonstrate that the shape of the Pt particles is only governed by the local CO pressure and is independent of the temperature and position of the reactor. Here, it is found that the transition toward a faceted particle shape is governed by a threshold value of around 85% conversion corresponding to a partial CO pressure of 25 mbar. That is consistent with previous reports [42, 89], showing that the shape of the Pt particles during CO oxidation is affected by the local CO pressure, such that the particles become more faceted at high rates of CO conversion. Moreover, Vendelbo et al. [42] demonstrated, based on DFT calculation, that a high partial pressure of CO will favor more open surface termination (211), whereas an atmosphere rich on O\textsubscript{2} will favor the closed (111) and open (211) surface termination more equally. The calculation implies that at lower CO pressure, the facet and step sites obtains a considerable O\textsubscript{2} coverage, which will stabilize the facets compared to the steps. That will result in a transition toward more faceted particle shapes, which is in perfect line with the findings observed in this study.

Since it now is clear that precautions must be taken when relating structure and activity, one can develop the present experiments to include different local densities and coverages of Pt to address the critical density of particles needed to maintain the high local conversion. Such experiments may also help to address if such effects are due to local temperature enhancements (hot spots) or to gas-phase communication among the particles.

Considering the findings from Chapter 4, it is obvious to question how the oxidation of the NR windows influence to the experiment. For the illumination conditions, the low areal electron dose rate is positive, as it was recommended to maintain it low to gain a longer operation time. For the primary electron energy it would be beneficial to go to 300 keV, however, that will compromise the sensitivity in the EELS measurements. Along the experiment the temperature is raised and the partial pressure of O\textsubscript{2} is decreasing as the conversion starts occurring. Both developments are positive in the light of the window oxidation, meaning that the window oxidation process will decay as the catalytic CO oxidation initiates. That being said, oxidation of the windows was observed during the experiments, however, its influence is assumed to be neglectable. That is because the amount of liberated nitrogen species is considerably smaller compared to the residual gas species present in the reactor. Thus, it is unlikely that it should influence on the EELS measurements nor the dynamics shape changes of the NPs. It was, however, speculated if the window oxidation could be accountable for the slight off-set in the local conversion, between the up-ramping and down-ramping measurements at 100 \textdegree C.
to 300°C in Figure 42, but no final explanation has been concluded yet.

5.9 CONCLUSION

A direct comparison between a local probing of the reaction environment (by TEM EELS) and a global integral of the catalytic conversion (by MS of the exit gas) is provided for a Pt loaded NR showcasing catalytic oxidation of CO. The comparison demonstrates considerable difference between the results of the two methods depending on the location in the reactor and the local density of Pt. Relating the observed structure of the NPs to the local and global measured conversion implies that the locally determined activity is a much better descriptor for the structural changes of the particles and reveals a local threshold value for the transformation towards faceted particles at 25 mbar of CO. The findings demonstrate that precaution is needed to relate structure and activity when using global integral of either the particle shape dynamics or gas composition.
ON THE STRUCTURAL DYNAMICS OF AN INDUSTRIAL-STYLE METHANOL CATALYST

In the previous chapter, the NR was used to relate the catalyst structure to its activity. By utilizing the NR, it was demonstrated how local structures must be related to the local environmental conditions that the catalyst is positioned in, such to avoid misinterpretations.

In this chapter, the demonstrated qualities of the NR will be employed while address on the dynamic structural behavior of an industrial style Cu/ZnO catalyst operating under high pressure conditions.
6.1 Introduction

Methanol, CH\textsubscript{3}OH or MeOH, is the simplest of the alcohols and is regularly used in industrial chemistry as raw material for other chemical processes, as formaldehyde, production of polymer with more [5, 69]. Today, MeOH is synthesized on an industrial scale from synthesis gas (or syn gas), containing H\textsubscript{2}, CO and CO\textsubscript{2} [5], and can be thermodynamically described by a combination of the following three reactions:

\[
\text{CO}_2 + 3\text{H}_2 \rightleftharpoons \text{CH}_3\text{OH} + \text{H}_2\text{O}; \quad \Delta H_{298K,50\text{bar}} = -49.8 \text{ kJ/mol} \quad (35)
\]

\[
\text{CO} + 2\text{H}_2 \rightleftharpoons \text{CH}_3\text{OH}; \quad \Delta H_{298K,50\text{bar}} = -90.7 \text{ kJ/mol} \quad (36)
\]

\[
\text{CO}_2 + \text{H}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O}; \quad \Delta H_{298K,50\text{bar}} = -40.9 \text{ kJ/mol} \quad (37)
\]

where Equation 35 and Equation 36 denote the production of MeOH and Equation 37 denotes the reverse water gas shift reaction [69].

In 2015, the global methanol demand reached 75 million metric tons and it is continuously increasing [90] as MeOH begins to be used for the production of transport fuels as a supplement to conventional petroleum-based fuels. The future outlook for MeOH shows promise, as MeOH synthesis is suggested as a way to store renewable energy and free mankind from its dependence on fossil fuels [91]. By capturing the CO\textsubscript{2} from the atmosphere and synthesizing it back into MeOH by use of sustainable energy, it is possible to close the carbon cycle [91, 92].

Today, the industrial synthesis of MeOH is performed at high pressure (50 bar to 100 bar) and 220 °C to 280 °C over a Cu/ZnO catalyst system [5, 93]. The Cu/ZnO-based catalyst has been investigated in detailed with a large range of techniques, revealing a dynamic structural-activity relationship of the catalyst within the high pressure regime [94, 95]. In addition, TEM has been used to visualize the structural-activity relationship of the Cu/ZnO system within the low pressure regime (1 mbar to 2 mbar) [27, 96]. It is therefore intriguing to try and replicate the TEM studies under higher pressure conditions (1 bar). This is still far from the industrial operation conditions of the catalyst, but is, however, comparable with the pressure regimes used in in situ photon experiments [94, 95]. Moreover, it has been indicated that formate species at the surface of the Cu/ZnO catalyst may play a significant role in the methanol synthesis [97]. The study furthermore implied that the coverage of formate would be more severe during lower temperature. Thus, it would be intriguing to employ the methodological approach from Chapter 5 to try to resolve the creation of formate at the surface.
6.2 METHOD

To investigate the structural dynamics of the Cu/ZnO system, an industrial-style catalyst prepared by co-precipitation methods was employed [98, 99]. The catalyst was dissolved in ethanol and loaded into the Dimes NR according to the loading procedure described in Section 2.2.4. After the loading procedure, the NR was mounted in the FEI Titan 80-300 ETEM microscope, where it was pumped to a base pressure of $\leq 10^{-5}$ mbar.

The microscope was operated with a primary electron energy of 300 keV and an areal electron dose rate below $250 \text{e}^{-/(\AA^2 \text{s})}$. Prior to the experiment, the image corrector was tuned to a $C_s$-value of $-10 \mu\text{m}$ to $-25 \mu\text{m}$ using an Au/C cross grating grid (Agar S106). The TEM images were recorded with the pre-GIF GATAN UltraScan 1000 CCD camera, which was calibrated towards the Au lattice fringes for HRTEM. Lower magnifications were calibrated using a Mag*I*Cal calibration standard grid.

The experiment was pursued according to the measurement scheme presented in Figure 46. Due to the complexity of the experimental plan, the measurement scheme is divided into 5 steps; initial state, reduction, activation, activity and final state. During the initial state, a region of interest (ROI) was located and documented at base pressure and 30 °C by TEM image at a low magnification, corresponding to an CCD pixel size between 0.88 nm to 0.065 nm, and at high magnification, corresponding with a pixel size of 0.064 nm to 0.039 nm. Here, the latter was used to attain high-resolution information from the catalyst. In addition to the ROI, an additional reference area located elsewhere in the reactor was monitored for later documentation of possible beam effects.

The experiment was initiated (marked as the reduction step in Figure 46) by introducing H$_2$ (purity 99.999 %) into the reactor at a pressure of 1 bar in the reactor zone. Here, the catalyst was reduced at 230 °C for an hour to reduce possible oxide layers on the Cu surface. During the final part of the reduction procedure, the ROI was monitored to document particle structure. Following the reduction step, CO$_2$ (purity 99.995 %) was added to the H$_2$ gas (activation phase) with a mixture ratio of H$_2$ : CO$_2$(1 : 1) to H$_2$ : CO$_2$(9 : 1). After the gas mixtures had time to equilibrate (a half hour was given), the ROI was monitored again, documenting the particle shape of the catalysts. Entering the activity phase, the temperature was slowly lowered to 100 °C using an ramp of 0.035 °C s$^{-1}$ to initiate the creation of formate. After the temperature had reach 100 °C and the system had stabilized for half an hour, the ROI was monitored once again. Finally, the temperature was dropped to 30 °C and the gas was pumped out (final state), before a final documentation of the ROI was done. Subsequently, both the initial reference area, which was monitored in the
The structural dynamics of an industrial-style methanol catalyst

Figure 46: Experimental procedure for the examination of the Cu/ZnO catalyst. Before initiating the experiment the ROI and reference area are examined under evaluated state at 30°C. The catalyst is reduced in 1 bar of H$_2$ at 230°C for around an hour, before introducing CO$_2$. After a half an hour with the mixture of H$_2$:CO$_2$ in the reactor, the temperature is slowly lowered to 100°C, using a ramp of 0.035°C s$^{-1}$. During all three steps, the ROI is monitored by TEM images. Finally, the NR is evacuated to the base pressure and the ROI, the initial reference area together with a new unilluminated area is monitored, to address possible influence of the electron beam.

6.3 Structural Transformation of the Cu/ZnO Catalyst

Figure 47 depicts the evolution of the catalyst structure along each step of the experimental procedure for a 1:1 mixture of H$_2$ and CO$_2$. For the first run displayed in Figure 47, no significant change is observed during the first steps (reduction and activation) of the experiment, but during the activity the catalyst undergoes a dramatic structural transformation. The restructuring is a dynamic process that keep on evolving during the entire examination at the activity state. As the reactor is evacuated to the base pressure and the temperature is lowered to 30°C, the dynamic restructuring of the catalyst stops and the catalyst remains in this "cauliflower" structure, as it is illustrated by the initial state of the second run in Figure 47. During the second run, the areal electron dose rate was lowered from 250 e$^-$/Å$^2$s to 100 e$^-$/Å$^2$s, after which the same experimental procedure was repeated. Entering the reduction step of the second run, the 'cauliflower' structure is reduced back to a structure similar to the reduced catalyst observed during the first run. Hereof, the catalyst demonstrates similar structural behaviour as for the first run, however, this time the structural transformation during activity is less severe compared to the first cycle.

If the reference areas are consulted (not shown here), it is seen that no such change in the catalyst structures is observed for the areas that stayed unilluminated during the experimental procedure. That strongly indicates that the structural transformation of the catalyst...
is induce by the electron beam. This suspicion is further strengthen when consulting Figure 48. Here, the restructuring of the catalyst under the activity step is displayed over a time period of 25 s of illu-minated at varying areal electron dose rates. Figure 48 demonstrates how vast restructuring occurs as the areal electron dose rate increases. Hence, it must be concluded that the structural changes of the cata-lyst are induced by the electron beam.

To gain insight into the beam induced structural changes and how to oppress them, the influence of the two gases is examined individually in Figure 49. The investigation follows the experimental procedure depicted in Figure 46, however, one of the gases is cut off from the NR during the activity step, resulting in a 500 mbar partial pres-sure of either H\textsubscript{2} or CO\textsubscript{2} inside the reactor zone, as illustrated by the overview scheme in Figure 49. It is clearly demonstrated by Figure 49 that the CO\textsubscript{2} is the root of the problem, as the structural changes of the catalyst only is observed in the pure CO\textsubscript{2} gas and not in the pure H\textsubscript{2} gas. Figure 49 also demonstrates how sensitive the catalyst is to the electron beam under the giving conditions, as an areal electron dose rate of only 1 e\textsuperscript{-}/(Å\textsuperscript{2}s) is use. Moreover, Figure 49 also demonstrates that the induced “cauliflower” structure can be reduced back to similar structures as for the initial state.

In the light of the findings above, the experiment is repeated with a significant lower areal electron dose rate (50 e\textsuperscript{-}/(Å\textsuperscript{2}s)) and with a gas mixture, where the partial pressure of CO\textsubscript{2} is reduces to a ten of
Figure 48: Influence of the areal electron dose rate on the structural formation of the CuZnO catalyst during activity. The displays illustrate the restructuring of the catalyst over 25 s while staying illuminated by the electron beam at four different areal electron dose rates. The TEM images are acquired during activity, meaning that the catalyst is exposed to $H_2:CO_2 = (1:1)$ and $100 ^\circ C$. The displays demonstrate how the restructuring is vastly dependent on the areal dose rate.

Figure 49: Influence of the single gases on the structural change of the CuZnO catalyst during activity. The overview illustrates the experimental procedure, accompanied by TEM images at each step, illustrating the structural transformation of the catalyst particles. During the activity of the first run, the $H_2$ gas is cut off from the NR, whereas for the second run it is $CO_2$ that is cut off. The TEM images are recorded with an areal electron dose rate of $1 e^-/Å^2 s$. 
the total pressure (100 mbar). Figure 50 displays the experimental results, showing only slight changes in the catalyst structure during the activity. The findings indicates the the restructuring of the Cu/ZnO catalyst can be oppressed by reducing the CO$_2$ partial pressure and the areal dose rate substantially.

6.4 DISCUSSION

The findings demonstrates how sensitive the the Cu/ZnO catalyst system is under the high pressure conditions of H$_2$ and CO$_2$. Especially towards the CO$_2$, the system reveals extreme sensitivity. These is probably due to a vastly larger inelastic cross-section of CO$_2$ in proportion to H$_2$, e.g. the total ionization cross-section is $\sigma_{\text{RBEB}}(\text{CO}_2, 300 \text{ keV}) = 1.87 \times 10^{-2} \text{ Å}^2$ compared to $\sigma_{\text{RBEB}}(\text{H}_2, 300 \text{ keV}) = 3.16 \times 10^{-3} \text{ Å}^2$, if using the relativistic binary-encounter-Bethe model [57, 58]. To oppress the beam effects, an areal electron dose rate less than $1 \text{ e}^-/(\text{Å}^2 \text{ s})$ is needed, if operating with a CO$_2$ partial pressure of 500 mbar. This is significant lower than seen for low pressure studies of similar system. For instant, Vesborg et al. reported on a threshold of $190 \text{ e}^-/(\text{Å}^2 \text{ s})$
for the differentially pumped system, below which a Cu/ZnO-based catalyst could be studied in CO$_2$ : H$_2$ = (50 : 50) at 2 mbar without disrupting the particle shape [96]. Conclusively, that means the beam effects are dependent of the type of gas but indeed also the pressure.

Figure 51: Summation of TEM time series for obtaining image signal. Illustration of cross-correlation alignment and summation strategy to attain image signals. The displays demonstrate the dilemma between attain sufficient signal for atomic resolution and avoiding beam induce effect. Summation at low signal images gets blurry due to specimen drift, where the summation of higher signal images gets blurry due to object changes.

To attain atomic structural information of the catalyst, an image signal of around 1000 e$^-$/Å$^2$ is needed, as a rule of thumb [100]. With an limitation of the areal electron dose rate at below 1 e$^-$/[(Å$^2$s), one must adopt a strategy based on summation of images to attain enough signal to resolve the atomic structure, as demonstrated in Figure 51. However, this will result in a summation of over 1000 images, which is insufficient in terms of image quality, as specimen drift and possible dynamic structural changes will blur out the image, as shown illustrated in Figure 51. There might be ways around the issue of specimen drift by using cross correlation alignment tools, however, these techniques again are limited by the image signal of each individual TEM image.

To gain insight into the atomic configuration of the Cu/ZnO catalyst at ambient pressure using the camera available (UltraScan 1000) seems rather challenging. A very low areal electron dose rate < 1 e$^-$/[(Å$^2$s) is necessary to oppress the beam induced restructuring while using a CO$_2$ : H$_2$ = (50 : 50) gas mixture. Thus, boosting the
camera detective quantum efficiency (DQE) [11, 101, 102] would be very beneficial for the further investigation. Another way to continue the investigation of the intrinsic structure dynamics of the Cu/ZnO-base catalyst would to reduce the partial pressure of CO$_2$, by which higher areal electron dose rates are allowed. Here, it was shown that the an areal electron dose rate of $50 \, e^-/s/\AA^2$ was approachable using a partial CO$_2$ pressure of 100 mbar. Even so better camera DQE would be favorable.

6.5 CONCLUSION

It has been shown that the Cu/ZnO-based catalyst demonstrates extreme sensitivity towards the electron beam while operating at 1 bar pressure of CO$_2$ : H$_2$. The findings indicate that CO$_2$ is accountable for the beam induced restructuring of the catalyst. To oppress the beam effects, the areal electron dose rate must be restricted to extreme low values, which inhibit the possibility of obtaining atomic structure information, or the partial pressure of CO$_2$ must be reduced considerably, which allows for higher areal electron dose rates permitting possible atomic information. In any of the two cases, a boost of the camera DQE would be favorable in the further investigation of the Cu/ZnO catalyst at ambient pressures.
CONCLUSION

This thesis has presented the nanoreactor (NR) system used in combination with transmission electron microscopy to visualize catalysts at work under conditions, which are identical to or approaching the real working condition for the catalyst. The NR is a nano-scale micro-electro-mechanical system (MEMS) device reactor based on silicon technology, which encases the catalyst and the gas from the microscope column by µm-thin membranes, in which electron-transparent SiN$_x$ windows are located and allow examination of the catalyst. Within the thesis, both advantages and shortcomings concerning the NR system have been elucidated and discussed. Here, each chapter has focused on addressing single relevant aspects regarding the use of the NR. In the following, a summary of the main findings and conclusions from each chapter is presented.

In Chapter 3, the aspect of attaining atomic resolution within *in situ* TEM studies was addressed. Here, it was illustrated how reducing the height of the gas phase, from 5.4 mm for the differentially pumped system to 2 µm to 5 µm for the NR system, in fact increases the ability to sustain the inherent resolution of the microscopy significantly. Specifically, it was demonstrated that 1 Å resolution could be maintained at 1 bar pressure within the NR, independent of the gas type applied (N$_2$, O$_2$, and Ar). In line with previous reports, it was shown that the total electron dose rate is determining for the image resolution attainable in the differentially pumped microscope, however, no such effect was observed for the NR system within the investigated regime (0.3 nA to 5.4 nA). Conclusively, the NR system demonstrates itself suitable for high-resolution imaging of catalysts immersed in a gaseous environment. Still, the NR windows will eventually give contributions to the final image as well as the fact that the windows may be reactive under the applied conditions, which needs to be considered.

Chapter 4 breaks with the common assumption that the Si-based electron-transparent windows of the NR are chemical inert, and demonstrates that this is rejected for an oxidizing atmosphere. Here, it was established that the SiN$_x$ windows undergo oxidation while illuminated by the electron beam. The findings reveals that both the operational conditions (pressure and temperature) as well as the illumination conditions (the areal electron dose rate and the primary electron energy) play a role for the integrity of the NR windows. In brief, precaution is needed when operating the NRs under oxidizing conditions.
Chapter 5 reports on the catalytic oxidation of CO over Pt NPs. The well-studied system was employed to challenge the common way that catalyst structure is related to the activity. A direct comparison between EELS probing of the local environment and global MS integral of gas exiting the reactor demonstrated significant variations in the results depending on the local density of Pt and the position in the reactor. Relating the local structural dynamics of the Pt particles to the local and global determined activity implies that the local measurement delivers a significant better descriptor for the shape changes, revealing that the transition toward more faceted particle structure is governed by the local CO pressure alone. The findings underline that precaution is needed to relate structure and activity of catalysts, especially when using global integral of the particle shape and/or activity.

In Chapter 6, the tools and knowledge achieved along the thesis were utilized to investigate the structural dynamics of an industrial-style Cu/ZnO-based methanol catalyst working under high pressure conditions (1 bar). The system revealed extreme sensitivity towards the electron beam during the presented conditions, resulting in dramatic beam induced structural changes. By modifying the gas composition and significantly lowering the areal electron dose rate, it was possible to reach a regime where the beam effects could be oppressed.

In short, the NR system offers the possibility to gain insight into the atomic dynamics and the local functionality of the catalyst, which are of the utmost importance for the understanding and development of new industrial catalysts. The NRs facilitate more realistic reactor conditions than for the conventional differentially pumped microscope, without compromising the atomic resolution. However, as it has been documented throughout this thesis, the NR and the catalyst might demonstrate considerable sensitivity towards the electron beam under such high pressure conditions. Therefore it cannot be stressed enough how important it is to have full control over the electron beam and its effect on the examined specimens.
Figure 52: Comparison of the oxidation of the nanoreactor windows at similar molar density of \( \text{O}_2 \) on the reactor. The oxidation levels display before (solid color) and after (faded color) the correction of the \( \text{O}_2 \) gas peak convolution as a function of the accumulated electron dose illuminated on the NR window. The first series (orange) is recorded at a \( \text{O}_2 \) pressure of 1000 mbar and a temperature of 500 °C, and is adopted from Figure 28. The second series (red) is recorded at an \( \text{O}_2 \) pressure of 500 mbar at 100 °C, and is adopted from Figure 32. The two series have a similar molar density of \( \text{O}_2 \). The oxidation rate for the two series is listed in the display.
Figure 53: Influence of the areal electron dose rate on the integrity of the nanoreactor windows - additional data at $100 \text{ e}^-/(\text{Å}^2\text{s})$ The displays shows the oxidation levels as a function of the accumulated electron dose illuminated on the NR window, acquired with an areal electron dose rate of $100 \text{ e}^-/(\text{Å}^2\text{s})$. The data are recorded on separate windows with a primary electron energy of 300 keV while exposed to an $\text{O}_2$ pressure of 500 mbar at 500 °C. Stars represent reference measurements recorded at evacuated state ($\leq 10^{-5} \text{ mbar}$).

Figure 54: Influence of the areal electron dose rate on the integrity of the nanoreactor windows - additional data at $1000 \text{ e}^-/(\text{Å}^2\text{s})$ The displays shows the oxidation levels as a function of the accumulated electron dose illuminated on the NR window, acquired with an areal electron dose rate of $1000 \text{ e}^-/(\text{Å}^2\text{s})$. The data are recorded on separate windows with a primary electron energy of 300 keV while exposed to an $\text{O}_2$ pressure of 500 mbar at 500 °C. Stars represent reference measurements recorded at evacuated state ($\leq 10^{-5} \text{ mbar}$).
Figure 55: Pt particle morphology as a function of the local and global measured conversion depending on the position and coverage of the reactor. The displays show the local measured conversion as a function of the global, where the color of each point represent the mean morphology factor measured at the very same area as the local conversion. The color scale rank from $\alpha = 0.79$ (black) to $\alpha = 1.67$ (bright green). The local and global conversion are also given in measure of CO partial pressure. The data is adopted from Figure 45 and divided into categorizes of coverage and position of the reactor. The displays demonstrate how the relation between the local and global conversion depends on the position and the coverage of the reactor.


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