Thesis for the degree of Doctor of Philosophy

## Quantitative Electron Microscopy Studies of Metal Nanoparticle Catalysts: Nanostructure, Support Interaction and Ageing Effects

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#### Cover image:

Upper left: STEM images of a cross-sectional Pt-Pd/Al<sub>2</sub>O<sub>3</sub> catalyst specimen. The size distribution of Pt-Pd NPs depends on the distance to the edge of the alumina support. More information in Section 4.1. From [1]. Upper right: Averaged STEM image of the interface between a Pt NP and ceria support. The atomic structure of both materials is clearly resolved. More information in Section 4.5. Center: Averaged STEM image of a Pt NP supported on  $\gamma$ -alumina. The atomic structure is resolved and three grains can be seen. More information in Section 4.5. Lower left: CO conversion versus temperature curves of fresh and aged Pt-Pd/Al<sub>2</sub>O<sub>3</sub> catalysts. The activity decreases with increasing ageing temperature. More information in Section 4.2. From [1]. Lower right: Strain map of a Pt NP supported on  $\gamma$ -alumina. A high concentration of large strains can be seen at the interface between the NP and the support. More information in Section 4.5.

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## Abstract

Heterogeneous catalysis plays a major role in modern society, for example in chemical production, sustainable energy production and emission control technologies. Metal nanoparticles (NPs) supported on oxide materials are frequent catalytic systems in this field. Although used and investigated for decades, open questions about the structure of supported catalysts and correlation with their catalytic properties remain. Some of these questions involve the three-dimensional structures of the catalysts, which become increasingly accessible by modern characterisation techniques, as well as the nanoscale structures down to the atomic level.

In this work, we focused on both of these aspects. We developed a specimen preparation method to reveal the three-dimensional structures of supported NP catalysts using transmission electron microscopy (TEM). We also refined the imaging of the catalysts' structures in the size range of a few nanometres down to individual atoms by using high-resolution dark-field scanning TEM (STEM) imaging, reaching a precision of 2 pm.

Structural aspects that were investigated included sintering (e.g. coalescence) of NPs in realistic catalysts at different temperatures and in different gas atmospheres, as well as sintering of NPs on model systems to investigate the effect of support surface corrugation. We used the developed specimen preparation method to study the three-dimensional distribution of NPs on the oxide support in a realistic catalyst as a function of ageing temperature. The structural properties were correlated to the catalytic activity, which was evaluated using a continuous flow reactor and simulations. The interaction at the interface between NPs and different support materials was studied by STEM imaging. The high spatial precision of 2 pm enabled the measurement of strain distributions within supported NPs and at external interfaces.

This work has given new insights into the detailed three-dimensional nanoscale structure of some of the most commonly used supported catalysts and improved the understanding of the relation between their structural properties and catalytic activity. The observation of interfacial strain indicates the possibility to tailor the catalytic activity by tuning the NP-support interaction.

**Keywords:** supported nanoparticle catalyst; transmission electron microscopy (TEM); scanning electron microscopy (SEM); FIB/SEM; particle size distribution (PSD); specimen preparation; ageing; strain; CO oxidation; platinum

## List of appended papers

This thesis is based on the following papers:

#### Paper I

The effect gas composition during thermal aging on the dispersion and NO oxidation activity over  $Pt/Al_2O_3$  catalysts Xavier Auvray, Torben Pingel, Eva Olsson and Louise Olsson Applied Catalysis B: Environmental 129 (2013) 517

#### Paper II

Revealing local variations in nanoparticle size distributions in supported catalysts: a generic TEM specimen preparation method Torben Pingel, Magnus Skoglundh, Henrik Grönbeck and Eva Olsson Journal of Microscopy 260 (2015) 125

#### Paper III

Pt Nanoparticle Sintering and Redispersion on a Heterogeneous Nanostructured Support Pooya Tabib Zadeh Adibi, Torben Pingel, Eva Olsson, Henrik Grönbeck and Christoph Langhammer The Journal of Physical Chemistry C 120 (2016) 14918

#### Paper IV

Three-Dimensional Probing of Catalyst Ageing on Different Length Scales: A Case Study of Changes in Microstructure and Activity for CO Oxidation of a Pt-Pd/Al<sub>2</sub>O<sub>3</sub> Catalyst Torben Nilsson Pingel, Sheedeh Fouladvand, Marc Heggen, Rafal E. Dunin-Borkowski, Wolfgang Jäger, Peter Westenberger, Daniel Phifer, Jace McNeil, Magnus Skoglundh, Henrik Grönbeck and Eva Olsson ChemCatChem (2017), DOI: 10.1002/cctc.201700479

#### Paper V

Influence of Strain Patterns on Catalytic Activity of Supported Nanoparticles Torben Nilsson Pingel, Mikkel Jørgensen, Andrew B. Yankovich, Henrik Grönbeck and Eva Olsson In manuscript My contributions to the appended papers:

Paper I: I performed the TEM experiments. The evaluation and interpretation of the TEM results were carried out together with my co-authors.

Paper II: I performed all the experimental work, interpreted the results together with my co-authors, wrote the first draft and wrote the manuscript together with my co-authors.

Paper III: I was involved in the experimental design of the TEM measurements and performed these together with my co-authors. I assisted in the evaluation and interpretation of the experimental results, as well as the revision of the manuscript.

Paper IV: I planned and performed the catalyst ageing procedure. The TEM specimen preparation and all SEM and TEM imaging experiments as well as corresponding data analysis were conducted by me. Catalytic activity tests as well as STEM EDX mapping were conducted in collaboration with my co-authors, data evaluation was performed by me. FIB/SEM slice & view tomography was performed by my co-authors, I was involved in the data evaluation. I wrote the first draft and wrote the manuscript together with my co-authors.

Paper V: I proposed a model system to elucidate the interaction at the NP-support interface. I performed the catalyst synthesis and all TEM experiments. Data treatment and interpretation was conducted together with my co-authors. I wrote the manuscript together with my co-authors.

In addition to the above papers, I contributed to the following papers which are not included in this thesis:

Mechanisms behind sulfur promoted oxidation of methane Djamela Bounechada, Sheedeh Fouladvand, Lisa Kylhammar, Torben Pingel, Eva Olsson, Magnus Skoglundh, Johan Gustafson, Marco Di Michiel, Mark A. Newton and Per-Anders Carlsson Physical Chemistry Chemical Physics 15 (2013) 8648

Methane Oxidation Over Pd Supported on Ceria–Alumina Under Rich/Lean Cycling Conditions Sheedeh Fouladvand, Stefan Schernich, Jörg Libuda, Henrik Grönbeck, Torben Pingel, Eva Olsson, Magnus Skoglundh and Per-Anders Carlsson Topics in Catalysis 56 (2013) 410

On the performance of  $Ag/Al_2O_3$  as a HC-SCR catalyst – influence of silver loading, morphology and nature of the reductant Hannes Kannisto, Kalle Arve, Torben Pingel, Anders Hellman, Hanna Härelind, Kari Eränen, Eva Olsson, Magnus Skoglundh and Dmitry Yu. Murzin Catalysis Science & Technology 3 (2013) 644

Thermodynamics of hydride formation and decomposition in supported sub-10 nm Pd nanoparticles of different sizes Carl Wadell, Torben Pingel, Eva Olsson, Igor Zoric, Vladimir P. Zhdanov and Christoph Langhammer Chemical Physics Letters 603 (2014) 75

Plasmonic Nanospectroscopy of Platinum Catalyst Nanoparticle Sintering in a Mesoporous Alumina Support Pooya Tabib Zadeh Adibi, Torben Pingel, Eva Olsson, Henrik Grönbeck and Christoph Langhammer ACS Nano 10 (2016) 5063

Functionalization of SSZ-13 and Fe-Beta with Copper by  $NH_3$  and NO Facilitated Solid-State Ion-Exchange

Alexander Shishkin, Soran Shwan, Torben Nilsson Pingel, Eva Olsson, Anna Clemens, Per-Anders Carlsson, Hanna Härelind and Magnus Skoglundh Catalysts 7 (2017) 232

## Preface

The research presented in this thesis was carried out in the Division of Microscopy and Microanalysis and in the Eva Olsson Group in the Department of Physics, as well as in the Competence Centre for Catalysis (KCK), Chalmers University of Technology, Gothenburg, Sweden, during the periods of September 2011 to December 2015 and August 2016 to August 2017. The work was performed under the supervision of Prof. Eva Olsson and co-supervisors Prof. Magnus Skoglundh and Prof. Henrik Grönbeck.

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## **1** Introduction

Heterogeneous catalysis is a key technology in today's society. Supported nanoparticle (NP) catalysts are commonly used in chemical production [2,3], energy applications [4] and environmental control technologies [5]. These catalysts consist of transition metal NPs dispersed on porous support materials, typically metal oxides. While the NPs catalyse chemical reactions, the support material provides a large surface area and stabilises the NPs. To develop efficient catalysts and use their expensive materials economically, profound knowledge of their structure from the macroscopic to the nanoscopic scale is crucial. This knowledge needs to be combined with an understanding of how structural characteristics influence the catalytic properties.

Catalyst deactivation is one of the major research topics in catalysis [6]. It denotes processes under which catalysts lose activity due to the temperatures and chemical environments they are exposed to during their operation. NP sintering (coalescence of NPs and/or atomic migration between NPs) is one of these processes. The severity with which NP sintering occurs depends on various factors, for example the operational temperatures, the materials of the NPs and the support [7,8] and the gas environment [9–12]. Because of deactivation, manufacturers need to design catalysts that perform well above their specifications when freshly produced. This increases the cost of the catalysts and the consumption of rare noble metals.

A variety of characterisation methods have been used to investigate catalytic NPs and NPs sintering, among them are gas adsorption / desorption experiments [13–18], various spectroscopy methods [19–21] and diffraction techniques [22–26]. These methods have in common that they average over large amounts of a catalyst sample, which results in good statistics due to many probed NPs, but do not offer spatially resolved information. The most versatile techniques for direct observation of individual NPs include scanning electron microscopy (SEM) and transmission electron microscopy (TEM) [27–30]. While SEM is an appropriate tool to investigate relatively large NPs, TEM is needed to image small NPs, clusters and single atoms of the catalytically active material.

The scope of this work is to further explore nanostructural aspects of supported NP catalysts and make correlations to their catalytic activities. Special effort was made to perform quantitative analyses whenever possible. We characterised supported NPs using different methods, with electron microscopy techniques like scanning TEM (STEM), SEM and focused ion beam SEM (FIB/SEM) constituting the cornerstones of our toolbox. We developed an advanced TEM specimen preparation

method which, due to the cross-sectional geometry of the specimens, allowed us to study the three-dimensional structure of supported NP catalysts before and after ageing, along with their catalytic activity. The influence of the gas atmosphere during ageing on the sintering of supported NPs was investigated, as well as the impact of a support with controlled structural inhomogeneity on NP sintering. We also studied strain in supported NPs on the atomic scale with picometre precision and performed kinetic simulations to determine the effect on the catalytic properties.

This thesis is structured in the following way: Chapter 2 describes the basic concepts of heterogeneous catalysis, NP catalysts, catalyst deactivation and automotive catalytic converters. In Chapter 3, the investigated catalytic systems as well as experimental methods used in this work are introduced. Chapter 4 contains a summary of the main results obtained during our work, the full details are found in the appended papers. Finally, conclusions and an outlook are presented in Chapter 5.

## 2 Heterogeneous catalysis and deactivation

Catalysis describes a phenomenon that increases the rate of a chemical reaction due to the presence of a catalytic material. It does so by offering an energetically more favourable reaction pathway compared to the non-catalysed reaction. The catalyst itself is not consumed in the catalytic reaction, so after each reaction cycle it is available to catalyse the next reaction.

Catalysts can have many different morphologies, ranging from atoms, molecules and NPs to larger structures like enzymes or solid surfaces. Catalysts can also have different phases and surroundings and are usually divided into three main categories: Homogeneous catalysts, where the reactants and the catalyst are in the same phase, heterogeneous catalysts, where the catalyst is solid and the reactants are gaseous or liquid, and biocatalysis, where enzymes catalyse chemical reactions.

In this chapter, heterogeneous catalysts, which are the focus of this thesis, will be introduced in more detail. After a general introduction, NP catalysts and methods to investigate them, as well as catalytic CO oxidation, one of the key reactions of heterogeneous catalysis, will be described. The next section provides an overview of different catalyst deactivation mechanisms. Finally, the more specific topics of automotive catalytic converters and bimetallic Pt-Pd catalysts will be discussed.

## 2.1 Heterogeneous catalysis

In heterogeneous catalysis, the catalyst is most commonly in the solid phase, whereas the reactants and products of the chemical reaction are liquid or gaseous. In the following, gaseous reactants and products will be discussed as this is the typical situation in environmental control catalysis. During a catalysed reaction, the reactants adsorb onto the catalyst surface individually and dissociate if necessary. They then react and form a product that desorbs from the surface. Afterwards, the catalyst is unchanged and available for the next reaction.

The catalyst surface can be considered as a number of discrete active sites which are capable of adsorbing the reactants, intermediates and products. Since a certain number of sites is occupied for each reaction, the total number of available active sites is one of the factors that limit the total reaction rate. A simple catalysed reaction of the reactants  $A_2$  and B to the product AB can be expressed in the following elementary steps (\* denotes an active site and A\* an adsorbed intermediate of species A):

$A_2 + * \rightleftharpoons A_2 *$	Adsorption of reactant $A_2$	(2.1)
$A_2 * + * \rightleftharpoons 2A *$	Dissociation of reactant $A_2$	
$B + * \rightleftharpoons B *$	Adsorption of reactant B	
$A * + B * \rightleftharpoons AB * + *$	Reaction of intermediates to product AB	
$AB* \rightleftharpoons AB + *$	Desorption of product AB	

This type of reaction, where all the reactants are adsorbed onto and in thermal equilibrium with the catalyst surface, is called *Langmuir-Hinshelwood* reaction [31]. An important example for this type of reaction in environmental control catalysis is the oxidation of carbon monoxide (CO) to carbon dioxide (CO<sub>2</sub>). A schematic view of this reaction, along with a corresponding energy diagram, is shown in Figure 2.1.



Figure 2.1: Schematic of the elementary steps of a catalysed Langmuir-Hinshelwood reaction between CO and  $O_2$  forming  $CO_2$  on a PGM catalyst. As the energy diagram in the center shows, an activation energy  $E_a$  has to be overcome for the reaction to proceed. The activation energy for the catalysed reaction is about five times lower than for the non-catalysed reaction, resulting in a higher reaction rate.

As can be seen in the energy diagram, an activation energy  $E_a$  is needed for the reaction between CO and O to proceed, whereas no activation energy is associated

with the adsorption of the reactants and the dissociation of oxygen. The activation energy  $E_a$  for the catalysed CO oxidation reaction is about  $100 \text{ kJ} \cdot \text{mol}^{-1}$ , whereas an energy of around  $500 \text{ kJ} \cdot \text{mol}^{-1}$  is associated with breaking the O-O bond in the non-catalysed reaction [31]. This demonstrates the main function of the catalyst for this reaction: It adsorbs and splits the oxygen molecules, which is the energetically most unfavourable step in the non-catalysed reaction, lowering the overall activation energy for the reaction. In this way, the catalyst increases the reaction rate considerably.

There are several conditions that a catalyst needs to fulfil in order to be suitable for a certain reaction. All reactants need to adsorb easily onto the catalyst, but no reactant may adsorb so strongly that it covers too much of the surface and inhibits the adsorption of the other reactants (so-called poisoning). Equivalently, the product of the reaction must only be loosely bound to the active sites, otherwise it might not desorb easily enough and poison the catalyst, hindering adsorption of the reactants.

### 2.2 Nanoparticle catalysts

The most commonly used metals for heterogeneous catalysts are found in the groups 8-11 of the periodic system. Since the catalytic reactions occur on the surfaces of these metals, their surface-to-volume ratio needs to be maximised in order to use the catalytic material efficiently and economically, as well as to reduce the space requirement of the catalyst. This is especially true for expensive noble metal catalysts. A large surface area can be obtained by using small metallic NPs. A similar property to the surface-to-volume ratio is the dispersion of the metal, which describes the ratio between the number of surface atoms and the total number of atoms of the metal.

The NPs are commonly dispersed onto a mostly inert porous support material that has a high surface area per volume. This ensures that the surfaces of the NPs are accessible to the reactants. The support also has the purpose to stabilise the NPs, which are prone to sintering under operating conditions (see Section 2.4). The main preparation techniques for supported NP catalysts are impregnation and precipitation [32]. The synthesis methods used in this work are described in Section 3.1.

Investigating the structural properties of supported NP catalysts and linking them to their catalytic performance is challenging. Already when investigating single crystal model catalysts, multiple factors like the reactant gas composition, reaction temperature and differences in conditions between structural characterisation (possibly *ex-situ*) and catalytic evaluation need to be considered. The number of factors that need to be taken into account becomes considerably larger when investigating supported NP catalysts. These factors include the effect of NP size, inhomogeneous NP size distribution, interaction with different support materials, changes of the NP oxidation state, different active sites depending on NP morphology (different facets, edges, corners) and dependence of NP morphology on the interaction with the support. Many of these factors are interdependent which makes universal conclusions from individual experiments rare.

In order to obtain a better understanding of the impact of these different parameters on the catalytic properties, progressively advanced experimental studies have been performed and still need to be performed. Experimental methods to investigate averaged properties of NP catalysts include X-ray diffraction [22– 26], X-ray photoelectron spectroscopy [19], X-ray adsorption spectroscopy [21], temperature-programmed techniques [33], chemisorption [13–18] and vibrational spectroscopy [20]. Electron microscopy [27–30] is used to obtain spatially resolved information about a catalyst's structure and composition with high spatial resolution.

Ideally, experimental studies are combined with theoretical calculations and simulations that assist in the understanding and/or design of the experimental studies [34–36]. Development of new synthesis methods for catalysts with specific properties like uniform NP size distributions or shapes is beneficial when aiming to perform conclusive studies, since it eliminates some of the aforementioned variables [32, 37–40].

## 2.3 Catalytic CO oxidation

Catalytic oxidation of CO to  $CO_2$ , briefly introduced in Section 2.1, is often used as a prototypical model reaction for heterogeneous catalysis. Since the reaction serves as a benchmark to investigate catalytic processes, both experimentally and theoretically, while at the same time being of high relevance for environmental technologies, it is one of the most extensively investigated reactions in catalysis [41]. Advantages of CO oxidation as a probe reaction are that it has a single rate-limiting step and only one product, which also only weakly interacts with the catalyst. CO, a product of incomplete oxidation of carbon-containing compounds, is a toxic, colorless and odorless gas. It is generated in large amounts by the petroleum industry and in combustion engines.

In the (non-catalysed) homogeneous gas-phase reaction between CO and  $O_2$  splitting of the oxygen molecule into atomic oxygen is limiting the reaction rate, since it is the elementary reaction step with the highest activation energy, about  $500 \text{ kJ} \cdot \text{mol}^{-1}$  [31]. A catalyst provides an alternative reaction path with a lower energy barrier, as depicted in Figure 2.1. In this reaction path, the reaction between CO and oxygen is rate limiting with an activation energy of about  $100 \text{ kJ} \cdot \text{mol}^{-1}$ . Supported noble-metal NP catalysts are mainly used for catalytic CO oxidation in industrial applications.

The catalytic activity varies considerably between different catalyst formulations and depends largely on the operating conditions, especially the reaction temperature. The kinetics of catalytic CO oxidation are often dictated by competitive adsorption of the two reactants, CO and  $O_2$ . Only if both are adsorbed on the catalyst's surface in sufficient amounts and close proximity, the reaction can efficiently progress. CO usually adsorbs strongly on reactive surfaces at temperatures close to room temperature, thereby hindering the adsorption of oxygen and the progression of the reaction.

At elevated temperatures, CO partially desorbs so that oxygen can adsorb on the available active sites and the reaction rate increases considerably. If the temperature is raised further, the CO and  $O_2$  coverages become so low that the reaction rate decreases due to a lack of reactants on the catalyst's surface. Therefore, there is a temperature window in which a catalyst performs optimally for this reaction. This temperature window should coincide as closely as possible with the operating temperature of the catalyst. Since modern industrial processes and combustion engines are becoming increasingly efficient, the exhaust gases often have relatively low temperatures. A major challenge in catalytic CO oxidation is therefore to obtain sufficient activity at low temperatures.

Catalysts for cleaning of exhausts from combustion engines usually contain Ptgroup metals (PGM), most notably platinum, palladium and rhodium. Traditional PGM catalysts have excellent activity for CO oxidation at high temperatures, but struggle at low temperatures. The operating temperature needs to be above at least 100 °C in most practical cases [42, 43]. While gold NP catalysts are more active at low temperatures [44], their thermal stability is an issue for exhaust aftertreatment solutions [45]. Development is ongoing to reduce the operating temperatures of PGM for CO oxidation [43].

### 2.4 Catalyst deactivation mechanisms

A catalyst might be very active when it is freshly produced, but over time different deactivation mechanisms can deteriorate its performance, which is a major problem. In case of the European emission standard 'Euro 6', a passenger car needs to still fulfil the emission limits after 100 000 km or five years of use [46]. This means that a fresh automotive catalyst needs to be designed with a much higher initial activity, resulting in higher consumption of expensive noble metals like platinum, palladium and rhodium. Catalyst deactivation is usually linked to the loss of active sites for the chemical reactions. Most deactivation mechanisms can be classified as either thermal deactivation, which is caused by high-temperature exposure, or chemical deactivation, which is caused by certain chemical species in the exhaust gas. The main deactivation mechanisms will be introduced here.

#### Nanoparticle sintering

Figure 2.2a shows the typical structure of a fresh catalyst with small, well dispersed metal NPs inside a porous support material. The main cause of thermal deactivation is sintering of the metal NPs. Under the influence of heat, the size of the NPs increases, which decreases the surface-to-volume ratio of the catalytic material, see Figure 2.2b.



Figure 2.2: Schematic view of different catalyst deactivation mechanisms. a) The catalyst in the fresh state, with small dispersed metal NPs on the porous oxide support. b) NP sintering: NP or atomic migration and coalescence leads to larger NPs with a lower total surface area. c) Washcoat sintering: At high termperatures the washcoat material can sinter, leading to blocked pores and a lower total accessible surface area. d) Poisoning: Chemical substances can selectively block active sites by adsorption or chemical reactions. e) Masking / Fouling: Contaminations (e.g. carbon) can non-selectively adsorb to the sample and block access to the active sites.

As mentioned in Section 2.5, the chemical reactions occur only on the surface of catalysts, so particle sintering will usually decrease the catalytic activity. The driving force for sintering is the reduction of surface energy and number of undercoordinated atoms. The temperature at which particle sintering occurs and the degree of sintering vary depending on materials [7,8] and gas environments. Water vapour has been shown to promote the sintering process [9–12]. The sintering onset temperature lies usually well within the temperature range that the catalyst is exposed to during normal usage. Most studies suggest an onset for severe platinum NP sintering on  $\gamma$ -alumina in oxidising environments at about 550-600 °C [9,47].

There are two different mechanisms of particle sintering, namely particle migration and coalescence, where entire NPs migrate over the support, and atomic migration, where individual atoms migrate from smaller to larger NPs via diffusion on the support or vapour phase transport. Several studies have been performed to investigate which of these mechanisms is the dominant in different situations, both on flat model systems [29, 48–50] and on more complex structures [29, 51, 52]. Although conclusions about the sintering mechanism could be drawn in some cases, a general prediction for the behaviour of other systems under different conditions appears to be difficult.

#### Support sintering

A different thermal deactivation mechanism is sintering of the catalyst support structure. The pore structure of the support can change, resulting in total or partial blockage of some pores, rendering active sites inside these pores unavailable or increasing the pore diffusion resistance for the gas. Figure 2.2c shows a schematic image of a catalyst after pore (and NP) sintering. Sintering of the support material usually requires higher temperatures than NP sintering. Support sintering can also involve a change in the crystal structure of the support material, which often induces a loss of total surface area and active sites.

In case of the most common support material,  $\gamma$ -alumina, a first phase transformation occurs when heating to around 800 °C to  $\delta$ -alumina, then at about 1000 °C to  $\theta$ -alumina and finally at around 1100 °C to  $\alpha$ -alumina, the most stable phase with only about 2% of the original surface area [5]. Heating to temperatures close to 1100 °C has therefore to be avoided under all circumstances. For certain support materials, adding stabilisers like La<sub>2</sub>O<sub>3</sub> can help to reduce the rate of support sintering.

#### Poisoning

Poisoning is a chemical deactivation mechanism. It describes a process where a chemical compound in the gas phase interacts with the catalyst and decreases its activity. Some poisons like lead can chemically react with the metal NPs, forming a catalytically inactive alloy, while others like  $SO_2$  chemisorb onto the NPs, blocking active sites on the surface and thereby decreasing the activity [5]. Figure 2.2d shows a situation where the catalytic NPs are partly covered by an adsorbed poison.

Another poisoning mechanism is the reaction of the support material with a poison, which can result in partial pore blocking.

Poisoning can be reversible in some cases. Desulfation of a catalyst is usually carried out at high temperatures, above  $600 \,^{\circ}$ C, under rich conditions, where CO and H<sub>2</sub> can reduce sulfate species formed under lean conditions [53]. Additionally, the support material can be modified to improve SO<sub>2</sub>-poisoning resistance [54].

#### Masking/Fouling

Masking or fouling is a deactivation mechanism similar to poisoning, but does not specifically affect certain components. Instead, contaminants like carbon physically cover parts of the pore structure and the catalytic NPs, thereby hindering the exhaust gas to reach the active sites. Figure 2.2e shows an illustration of a masked catalyst.

#### Loss of catalytic material

Apart from poisoning a catalyst, gas phase species can also react with catalytic components, form volatile compounds and leave the catalyst, resulting in a loss of catalytic material [6].

### 2.5 Automotive catalytic converters

In the exhaust aftertreatment system of a petrol engine, three chemical reactions need to occur in order to remove the most hazardous components from the engine exhaust: carbon monoxide needs to be oxidised, different hydrocarbons (HC) need to be oxidised and nitrogen oxides (NO and NO<sub>2</sub>, summarised as NO<sub>x</sub>) need to be reduced. The non-balanced reactions are:

$$CO + O_2 \rightarrow CO_2$$

$$HC + O_2 \rightarrow CO_2 + H_2O$$

$$NO_x + CO \rightarrow N_2 + CO_2$$
(2.2)

Noble metal NPs, mainly consisting of platinum, palladium and rhodium, have proven very effective for these reactions and are used in the so-called *three-way catalytic converter* (TWC), which is the most widespread solution for exhaust aftertreatment in passenger cars with petrol engines today [55]. All three reactions mentioned above occur simultaneously in the TWC. To make this possible, it is important that the air-to-fuel ratio in the exhaust gas composition is held very closely to the stoichiometric ratio, which is 14.7:1. At the stoichiometric ratio, the provided air is precisely sufficient to burn all of the harmful components. If the oxygen concentration is higher, too much carbon monoxide will be oxidised, deteriorating the NO<sub>x</sub> reduction. With less oxygen the NO<sub>x</sub> will be reduced efficiently, while carbon monoxide and hydrocarbons will not be oxidised to the full extent. The correct stoichiometric composition is achieved by using an oxygen sensor, a so-called  $\lambda$ -sensor, that regulates the injection system of the engine.

The most common support materials in automotive converters include  $\gamma$ -alumina  $(Al_2O_3)$ , silica  $(SiO_2)$ , zirconia  $(ZrO_2)$  and ceria  $(CeO_2)$ . The dispersion of the metallic NPs onto the support is usually achieved by wet impregnation [56]: The support material in powder form is soaked in an aqueous solution containing a precursor (salt) of the catalytic element. Electrostatic and capillary forces distribute the salt over the entire surface of the support material where it adsorbs or ion exchanges, given that the precursor salt and pH condition were chosen correctly for the respective support material. Afterwards, the impregnated catalyst support is dried and subsequently calcined at a temperature typically around 400-600 °C to remove salt residues. To hold the impregnated support material in place and allow a good gas flow with low pressure drop through the catalytic converter, the catalyst powder is washcoated onto a monolith structure composed of parallel and uniform channels. The monolith can be composed of metallic or ceramic materials, most commonly cordierite. The thickness of the washcoat layer is on the order of tens of micrometres. Figure 2.3 shows the structure of a catalytic converter at different length scales.

As today's car manufacturers push towards the most fuel efficient engines possible [57], lean-burn and especially diesel engines have become popular on the European market, with diesel cars accounting for 52% of all new registrations in 2015 [58,59]. There has, however, been a decline in market shares since then [60, 61], possibly connected to the recent diesel emission scandal [62–65]. The exhaust from diesel engines contains a higher amount of oxygen compared to the stoichiometric airto-fuel ratio of 14.7:1. It lies typically around 20:1 [31]. As mentioned earlier, a higher oxygen content in the exhaust leads to a decreased NO<sub>x</sub> conversion in the TWC, resulting in higher NO<sub>x</sub> emissions. This is a central limitation of the TWC: Although the TWC has had enormous success in improving the exhaust quality of cars over decades, it cannot be directly applied for NO<sub>x</sub> abatement for lean-burn and diesel engines.

Due to the strong negative effects of  $NO_x$  in the atmosphere, including acid rain and the risk of respiratory illnesses [66, 67], in many countries laws are in place to regulate the maximum amount of  $NO_x$  emission permitted from vehicles. Figure 2.4 shows the development of the European regulations for the emissions of  $NO_x$  and particulate matter (PM) for diesel passenger cars between 1992 and 2014 (with the latest regulation still in place at the time of writing). Similar regulations are in place for different vehicle types and in different regions of the world. From 1992 to 2014 the maximum amount of  $NO_x$  emitted from a diesel passenger car was reduced



**Figure 2.3:** Structure of an automotive catalytic converter at different length scales: Gas flows through a monolithic channel structure (blue arrow), the channel walls are coated with a washcoat material. The washcoat consists of porous oxide support particles, in which the catalytically active NPs are dispersed.

from 970 mg/km to 80 mg/km [46,68–70].

In order to fulfil these stringent regulations, alternative solutions need to be used for  $NO_x$  abatement for lean-burn and diesel engines. One solution for passenger cars is the  $NO_x$  storage and reduction (NSR) catalyst [53, 71, 72]. The basic idea behind the NSR catalyst is to store the  $NO_x$  inside the catalytic converter during the time when the exhaust conditions do not allow an efficient conversion. This is done by addition of barium oxide (BaO) to the washcoat layer. Under oxidising conditions, BaO effectively stores  $NO_2$  by forming barium nitrate  $(Ba(NO_3)_2)$  on the surface.

The  $NO_x$  is stored when the engine is run under lean conditions for several minutes, until a short fuel rich pulse of a few seconds is initiated during which the exhaust contains less oxygen. During this pulse, components like hydrocarbons, CO and H<sub>2</sub> are able to reduce the stored nitrate species to nitrogen. The engine is thereafter switched back to lean mode and a new NO<sub>x</sub> storage cycle begins. Overall, the engine is run in lean mode, although the short rich pulses give a small fuel penalty.

An alternative solution for the removal of  $NO_x$  is selective catalytic reduction (SCR), where a reducing agent is added to the exhaust gas in order to selectively



Figure 2.4: European emission legislation for diesel passenger cars from 1992 to 2014. Shown are the regulations for  $NO_x$  and particulate matter (PM). Data from references [46,68–70].

reduce  $NO_x$ . An SCR catalyst does usually not require noble metals, but instead uses base metals or metal-exchanged zeolites as the catalytically active material [5].

## 2.6 Bimetallic Pt-Pd catalysts

Often, more than one catalytic component is used in automotive catalytic converters. A popular choice is the addition of Pd to a Pt catalyst. Several reasons could motivate such a decision, either the properties of the bimetallic catalyst could be better than the pure systems, or the price of the catalyst could be reduced by adding a cheaper component while using less of the more expensive one. Several studies have addressed the properties of bimetallic Pt-Pd catalysts.

It was generally observed that Pt-Pd catalysts show a lower degree of NP sintering compared to corresponding monometallic Pt or Pd catalysts, the addition of Pd seems to have a stabilising effect on the NPs [47, 73–75]. Studies of the catalytic activity for CO and hydrocarbon oxidation show a slightly better performance of the Pt-Pd system [76] and less degradation of the activity after ageing [73, 77].

An interesting aspect of bimetallic catalysts is the degree of alloying between the two components. The NPs can be monometallic with the two different particles (pure Pt and Pd) randomly distributed over the support, or the two metals can form bimetallic Pt-Pd NPs. In case of bimetallic NPs, two possible arrangements are homogeneous alloys and core-shell structures. In a core-shell NP, the component with the lower surface energy usually forms the shell of the NP. In an alloyed state, Pd can stay partly metallic even after high-temperature treatment in an oxidising atmosphere, even though some PdO nanocrystals have been observed around alloyed Pt-Pd NPs [73]. Studies have also shown that sintering usually leads to an increased

intermixing of Pt and Pd [74], while large NPs have exhibited a tendency to be rich in Pt compared to the nominal catalyst composition [78].

## 3 Materials and methods

In this chapter, the catalytic material and the experimental methods used for this thesis will be described. The experimental methods include routinely used methods like surface area measurement of the catalytic material by  $N_2$  physisorption, hydrothermal ageing and catalytic activity evaluation by CO oxidation. Additionally, catalyst characterisation by electron microscopy (scanning electron microscopy (SEM), focused ion beam / scanning electron microscopy (FIB/SEM) and scanning transmission electron microscopy (STEM)) will be described, including X-ray spectroscopy and the procedures for data treatment and analysis.

### 3.1 Nanocatalysts and preparation by impregnation

This section begins with an introduction to nanocatalyst preparation by wet impregnation, which is followed by specific information about the preparation methods that were applied in the appended papers.

A common method to produce supported NP catalysts is wet impregnation. A precursor salt that contains the catalytically active metal is dissolved and forms ions. The precursor solution is then added to the support material, which is usually present in powder form. The most common support materials are metal oxides that contain surface hydroxyl groups (X-OH, X = aluminium, silicon, cerium, ...) [79,80]. The hydroxyl groups can be used to improve the adsorption and disperion of the precursor ions on the support surface. In case of precursor cations, the pH of the solution can be decreased below the isoelectric point of the support material to form acidic surface sites (X-O<sup>-</sup>) which electrostatically attract the cations. If precursor anions are present, the pH can be raised to form basic surface sites (X-OH<sub>2</sub><sup>+</sup>) respectively.

A special case is incipient-wetness impregnation [32]. It implies that just the amount of precursor solution is added to the support material that is needed to fill up the available pore volume, without any excess solution that needs to be removed afterwards. This approach is very economical since all the catalytic material is dispersed inside the pores and waste is minimised. Since the amount of metal that can be impregnated on the support is limited with this method, several impregnation steps might be necessary if catalysts with high metal loadings need to be prepared. After the impregnation is performed, the support material is dried and subsequently calcined at temperatures of several hundred degrees Celsius to remove residues of the precursor salt. A drying method that is often applied is freeze-drying. The impregnated support material is cooled using liquid nitrogen and then warmed up in vacuum. The water them sublimes, which prevents that liquid water washes some of the catalytic material out of the pores during drying.

#### Paper I

The  $Pt/Al_2O_3$  catalyst used in Paper I was prepared by wet impregnation of a precursor solution containing platinum(II) nitrate  $(Pt(NO_3)_2, Heraeus GmbH, 15.46 wt.-\% Pt)$  onto  $\gamma$ -alumina powder (Puralox SBa-200, Sasol). The pH of the solution was adjusted to 2 by addition of diluted HNO<sub>3</sub>. Consequently, the impregnated powder was freeze-dried and calcined in air at 500 °C for 2 hours. The nominal platinum loading was 1 wt.-%.

#### Paper II and IV

In Paper II and IV, a commercially produced bimetallic Pt-Pd catalyst supported on  $\gamma$ -alumina was investigated. It corresponds to a commercial NSR catalyst in terms of Pt-Pd concentrations and the preparation method (based on wet impregnation), but was prepared without the NO<sub>x</sub> storage component in order to reduce the complexity and enable systematic studies of the NP sintering behaviour. The noble metal loadings of this catalyst were 0.17 wt.-% platinum and 0.03 wt.-% palladium, corresponding to an atomic Pt:Pd ratio of 3.1:1.

The catalyst sample was received in powder form, containing the impregnated alumina support agglomerates, which in turn were built up by small primary  $\gamma$ -alumina particles. The density of the powder sample was measured to about 0.6 g/cm<sup>3</sup>. The alumina agglomerates were typically in the size range of a few hundred nanometres to several micrometres.

#### Paper III

The catalyst sample investigated in Paper III consisted of platinum NPs on a nanostructured alumina support. The support was composed of a sputter-coated alumina layer on a flat  $Si_3N_4$  membrane. Additionally, alumina cones (diameter at the base around 80 nm) were nanofabricated onto the surface and covered by a sputter-coated alumina layer. The support did not have a porous character like the  $\gamma$ -alumina support used in the other studies. A thin platinum film with a nominal thickness of 0.5 nm was deposited onto the surface by e-beam evaporation. Thereafter, the sample was heated in argon to 600 °C for 10 minutes to form Pt NPs.

#### Paper V

In Paper V, supported platinum NPs on alumina and ceria were investigated. The synthesis of the catalysts was performed by incipient-wetness impregnation. An aqueous solution of tetraammineplatinum(II) nitrate  $((NH_3)_4Pt(NO_3)_2)$ , Alfa Aesar, 4 wt.-% Pt) was used as the platinum precursor and dropwise added to either  $\gamma$ -alumina or cerium(IV) oxide nanopowder (Sigma-Aldrich).

In order to improve the adsorption and dispersion of the platinum precursor cations  $([(NH_3)_4Pt]^{2+})$  on the support surface, the pH of the precursor solution was adjusted to 11 using a diluted ammonia solution under continuous stirring. The impregnated support was then freeze-dried using liquid nitrogen and afterwards calcined in air at 500 to 540 °C for 1 to 3 hours. The nominal platinum loadings of the catalysts were 4 to 6 wt.-% Pt for the alumina catalysts and 3 wt.-% Pt for the ceria catalyst.

## 3.2 Hydrothermal ageing

To simulate the conditions that a catalyst is exposed to during its lifetime in a catalytic converter of a vehicle, hydrothermal ageing in a gas flow reactor was performed at different temperatures. The gas flow reactor consists of a quartz tube containing the catalyst, which is surrounded by a metal coil for resistive heating. The tube can be sealed and gas with a defined composition can be fed through, controlled by mass flow controllers. Thermocouples are introduced into the sample to determine its temperature, the readout is used as feedback for the heating power supply in order to maintain the desired temperature.

For the hydrothermal ageing applied in Paper IV, the catalyst powder was loaded into a modified ceramic monolith (usually used for holding the washcoat layer as explained in Section 2.5) which was cut from one side to create an opening, while still allowing a reasonable gas flow around and through the powder. The total gas flow in the reactor did not exceed 1 L/min in order to keep the powder in place. Ageing was performed at 500 °C, 600 °C, 700 °C and 800 °C. The sample was heated up in pure argon at a rate of 7 °C/min. After that, it was exposed to an atmosphere of 75 vol.-% argon, 15 vol.-% oxygen and 10 vol.-% water vapour for 24 hours. Cooling was done in pure argon for at least two hours before the powder was removed from the reactor. Figure 3.1 shows the monolith filled with catalyst powder in the reactor tube and the reactor during ageing.

It should be noted that this synthetic ageing protocol does not simulate all aspects of real engine ageing in a vehicle. Although some key aspects like the oxidising environment (which is true most of the time in a real exhaust) and the presence of water vapour are reproduced, engine exhausts contain a variety of complex components [5] which can influence the ageing process. Also, the temperature profile can be different and more dynamic than in this simulated ageing. Despite these differences, studies have shown that synthetic ageing can reproduce many aspects of real vehicle ageing, especially when thermal effects on NP stability and sintering are the main concern [81].



Figure 3.1: a) Image of the modified monolith, filled with catalyst powder, in the reactor tube. The heating coil seen to the left covers the whole area during ageing. b) Image of the reactor during ageing at 800 °C.

## 3.3 Surface area measurements (BET method)

The total surface area of catalyst samples was determined by nitrogen physisorption at liquid nitrogen temperature followed by an evaluation after the Brunauer-Emmett-Teller (BET) method. Nitrogen was adsorbed onto the sample while the total adsorbed volumetric quantity of nitrogen  $\nu$  and the corresponding nitrogen partial pressure p were measured. Assuming layer-wise adsorption and no interaction between the layers, the BET equation is [5]:

$$\frac{p}{\nu \cdot (p_0 - p)} = \frac{c - 1}{\nu_m c} \left(\frac{p}{p_0}\right) + \frac{1}{\nu_m c}$$
(3.1)

with

$$c = e^{\frac{H_1 - H_L}{RT}} \tag{3.2}$$

where  $p_0$  is the saturation pressure at the used temperature, c is the BET constant,  $\nu_m$  is the volume adsorbed at monolayer coverage,  $H_1$  is the heat of adsorption of the first and  $H_L$  of the following monolayers, R the gas constant and T the temperature. If the left side of equation 3.1 is plotted against  $p/p_0$ , a linear plot is obtained. The assumption of such linear behaviour is usually valid in the range of 0.05  $< p/p_0 < 0.3$ . The slope *a* and y-intersect *b* of the curve can be measured in that range and the monolayer adsorbed gas quantity  $\nu_m$  can be calculated:

$$\nu_m = \frac{1}{a+b} \tag{3.3}$$

Now, the BET surface area can be calculated:

$$S_{BET} = \frac{\nu_m N s}{VM} \tag{3.4}$$

where N is Avogadro's number, s the adsorption cross section of a nitrogen molecule, V the molar volume of nitrogen and M the total mass of the catalyst sample. The measurements in this work were performed using a Micromeritics Tristar<sup>TM</sup>. Prior to the experiment, the specimens were degased in vacuum.

## 3.4 Catalytic activity evaluation: CO oxidation

The catalytic activity of fresh and aged samples in Paper IV was determined by CO oxidation experiments. The catalysts were coated onto ceramic monoliths by dipcoating using a washcoat slurry composition of 80% water, 16% catalyst powder and 4% böhmite. The monoliths were exposed to a heating gun for short times for drying and transforming the böhmite to alumina. A total amount of 200 mg washcoat (after drying) was used for each monolith. Afterwards, the monoliths were calcined in an oven at 500 °C for 60 minutes to stabilise the washcoat layer, improve the adhesion to the monolith and remove contaminations.

The monoliths were then inserted into a gas flow reactor similar to the one used for hydrothermal ageing (Section 3.2). The inlet gas to the reactor was controlled by gas flow controllers, heating was performed by resistive heating of a metal coil around the quartz tube, and the sample temperature was measured by thermocouples inserted into a central channel of the monolith. The outlet gas was analysed by a quadrupole mass spectrometer (Pfeiffer Prisma<sup>TM</sup>). During the experiments the reactor was insulated using glass wool to reduce heat losses and ensure an even temperature profile within the sample region.

Prior to the CO oxidation experiments, the samples were heated in pure argon to  $450 \,^{\circ}\text{C}$  using a heating rate of  $5 \,^{\circ}\text{C/min}$  and a total gas flow of  $500 \,\text{ml/min}$ .  $4 \,\text{vol.-\%}$  oxygen were added to the stream for 10 minutes to obtain a defined initial oxidation state for all samples. After this pretreatment, 1000 ppm CO and 4 vol.-% oxygen balanced with argon (total flow:  $500 \,\text{ml/min}$ ) were introduced into the reactor, and the outlet CO and  $CO_2$  concentrations were determined using the mass spectrometer. The CO-to-CO<sub>2</sub> conversion was calculated using the inlet CO and outlet  $CO_2$  concentrations.

The temperature was then reduced to 50 °C and increased to 450 °C two times, resulting in CO conversion measurements during two heating and two cooling ramps. Due to the possibly different oxidation and CO poisoning states at the beginning of the heating and cooling ramps, the conversion curves are usually slightly shifted with respect to each other (hysteresis-like behaviour). The measurements from the second cooling ramp were used for further evaluation.

### 3.5 Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) was used in this study to image oxide support particles as well as large Pt-Pd NPs (larger than 10 nm) and perform chemical analysis by means of X-ray spectroscopy. A short introduction to this technique is given in this section, for a more in-depth description see Goldstein et al. [82]. In an SEM, electrons are emitted from an electron source, usually a field-emission gun, and then accelerated by a high voltage. Typical electron energies are 0.1-30 keV. The electrons enter a system of two or more electromagnetic lenses which form an electron beam that is focused to a small spot, representing a demagnified image of the tip of the electron gun.

The surface of the specimen is placed in the plane of the cross-over of the focused electron beam. The electrons enter the specimen and interact through elastic and inelastic scattering in the so-called interaction volume, which can have dimensions up to several micrometres, depending on the acceleration voltage and specimen material. Different signals are created inside the specimen, and the depth from which they can escape the specimen and be detected depends on their mean free path inside the specimen material. The electron beam is rastered across the specimen surface using scan coils. The different signals that are generated from the interaction between the specimen and the electron beam can be recorded for each beam position, resulting in a two-dimensional representation of the specimen.

Secondary electrons (SEs) are created by inelastic scattering of the electron beam which ionises atoms in the material. The SEs have low energies, typically below 10 eV. With such low energies, the SEs are easily reabsorbed by the material. Only SEs created very close to the incident electron beam can escape the specimen and be detected, resulting in a very localised signal (within a few nanometres from the incident beam). SEs are usually used to obtain topographic information about the specimen, since the probability of SE emission is higher close to edges where the electrons can escape in more directions compared to a flat surface.

Backscattered electrons (BSEs) are created by elastic scattering of the incident electrons, so their energies are close the energy of the incident beam. The BSEs have a larger mean free path of up to around 100 nm (depending on their energy) and can therefore be created further away from the incident beam. BSEs can be used to obtain images with compositional contrast since the probability for elastic scattering increases with the atomic number of the atoms in the material. Regions with heavier atoms therefore create more BSEs, leading to a higher intensity in the image compared to regions with lighter atoms. BSEs can also create SEs at positions further away from the incident beam compared to the direct SE signal, but these SEs contribute mainly to a smooth background signal.

Characteristic X-rays constitute the third important signal in the SEM. They are created by radiative relaxation of atoms in the material, where electrons relax to a lower energy state in the inner electron shells. The energies of the X-rays can be analysed and used to identify and quantify chemical elements present in the specimen. The process of acquiring and evaluating X-ray spectra will be described in more detail in Section 3.9.

Figure 3.2 summarises the different signals and detectors most frequently used in SEM. The SEM results presented in this work were obtained using a Zeiss Ultra- $55^{\text{TM}}$  SEM operated at an acceleration voltage of 10 kV. A backscattered electron detector was used to obtain a clear image contrast of the Pt-Pd NPs within the alumina support. The X-ray spectra were acquired using a diode-type Si EDX detector (see Section 3.9).

# 3.6 Scanning transmission electron microscopy (STEM)

### 3.6.1 Imaging principle

For high-resolution imaging of catalytic NPs and chemical analysis using X-ray spectroscopy, STEM was applied. STEM is an imaging mode that can be performed in many commercial TEMs. A TEM uses an electron source and electron optics in front of the specimen similar to those in an SEM. The typical range of acceleration voltages is 60-300 kV. In contrast to the conventional TEM imaging mode, in which the microscope works similarly to a conventional light microscope and electromagnetic lenses below the specimen create an optical electron image (see reference [83]), in STEM mode the electron beam is focused to create a small probe in the plane of the specimen.

The electron probe is then scaned over the specimen. Instead of using the SE or BSE signals like in the SEM, the transmitted electrons are used in STEM mode to form an image. This implies that the specimen has to be very thin, from 10 nm to a few hundred nanometres, depending on the material and desired resolution and contrast. The incident electrons either pass through the specimen without interaction or they scatter elastically or inelastically. Electrons which are not scattered or



Figure 3.2: Schematic drawing showing the different signals commonly used in SEM. SEs are only detected if they are created within a few nanometres from the surface, whereas BSEs and X-rays can originate from a larger depth within the pear-shaped interaction volume.

scattered to small angles can be detected by a detector positioned on the optical axis. If these electrons are used, bright-field (BF) imaging is performed. In BF mode, the image shows mainly phase contrast like conventional TEM imaging [84]. If a concentric annular detector is used, which excludes the electrons close to the optical axis, annular dark-field (ADF) imaging is performed.

If the inner acceptance angle of the electron detector is larger than about 40 mrad, this technique is called high-angle annular dark-field (HAADF) imaging. Figure 3.3 shows a schematic overview of the incoming electron beam on the specimen and the different signals that can be used for imaging. When using large scattering angles, most of the scattering occurs very close to the nuclei of the scattering atoms, changing the Z-dependence (Z: atomic number of scattering atoms) of the scattering cross section compared to BF or ADF imaging. In HAADF, the scattering can be treated similarly to unscreened Rutherford scattering, which has a  $Z^2$  dependence of the scattering cross section. Due to screening by the electron cloud, the observed Z-dependence varies between  $Z^{1.6}$  and  $Z^{1.9}$  [85].

This means that an atom whose atomic number is twice as large as the atomic number of another atom scatters (nearly) four times as many electrons to high angles. The image contrast with respect to the chemical composition of the specimen is thus strongly enhanced by the atomic number dependence. HAADF imaging is therefore often called Z-contrast imaging. It can also be shown that HAADF imaging is characterised by many incoherent scattering characteristics, thereby minimising the image contrast mechanisms arising from Bragg scattering and interference [84]. This is especially useful when imaging metallic NPs supported on a support material that has a lower average atomic number. In conventional coherent imaging, interference effects from the support material can obscure the signal from the NPs. In HAADF mode, the coherent phase interference effects are suppressed and the NPs generate a clear signal due to the strong Z-dependence of the scattering. As the name indicates, HAADF-STEM is a dark field imaging mode. Since electrons that are scattered to high angles are detected, a point in an image is brighter the more scattering is caused by the specimen at that position. A hole in the specimen, which does not scatter any electrons at all, will therefore be black in an HAADF-STEM image, whereas thick or dense regions appear bright.

#### 3.6.2 Resolution and aberrations

The spatial resolution in STEM imaging is mainly limited by the achievable diameter of the focused electron beam on the specimen. The Rayleigh criterion can be used to approximate the beam diameter  $d_b$  and hence the best achievable resolution in STEM, assuming the beam diameter is only diffraction-limited [86]:

$$d_b \approx 0.61 \frac{\lambda}{\sin(\alpha)} \tag{3.5}$$

where  $\lambda$  is the wavelength of the electrons and  $\alpha$  the convergence semi-angle of the focused electron beam. The convergence semi-angle is mainly determined by the size of the beam limiting aperture above the specimen. The wavelength  $\lambda$  can be calculated using:

$$\lambda = \frac{h}{\sqrt{2m_0 eV\left(1 + \frac{eV}{2m_0c^2}\right)}} \tag{3.6}$$

where h is Plank's constant,  $m_0$  the electron rest mass, e the electron charge, V



Figure 3.3: Schematic drawing showing the convergent electron beam hitting the specimen and the different signals that can be used for STEM imaging. The angles are exaggerated for clearer illustration. BF: bright-field, HAADF: high-angle annular darkfield.

the acceleration voltage of the microscope and c the speed of light. For a 300 kV TEM, the electron wavelength is around 2 pm. Assuming a convergence semi-angle of 17.5 mrad, the approximated theoretical beam diameter and resolution limit is:  $d_b \approx 0.07$  nm.

This resolution, however, can often not be achieved in reality due to the imperfection of the magnetic lenses used in the TEM. Magnetic lenses have various aberrations which are limiting the resolution in modern (S)TEMs, among those are astigmatism, spherical aberration and chromatic aberration. Astigmatism results from not perfectly cylindrical magnetic fields in the lenses and leads to an elongation of the focused spot in a certain direction. Stigmators, which are octupoles that create a compensating field, can be used to relatively easy eliminate the effects of astigmatism.

Spherical aberration depicts the effect that off-axis electrons are stronger deflected towards the optical axis compared to electrons travelling close to the optical axis. A point object is imaged as a disc as a result of this aberration, leading to a degraded resolution. In the focal plane, the diameter of the disc caused by spherical aberration
can be approximated by [83]:

$$d_{sph} \approx C_s \alpha^3 \tag{3.7}$$

where  $C_s$  is called the spherical aberration coefficient of the magnetic lens. Since there is a strong dependence on the semi-convergence angle  $\alpha$  of the electron beam, spherical aberration becomes dominant when large beam limiting apertures are used. As decreasing the aperture size leads to less spherical aberration but more diffraction effects, there is an optimum aperture size or convergence angle to balance these two effects. The beam diameter after combining diffraction and spherical aberration can be approximated as:

$$d_b \approx \sqrt{\left(\frac{\lambda}{\sin(\alpha)}\right)^2 + (C_s \alpha^3)^2}$$
 (3.8)

leading to an optimum semi-convergence angle of  $\alpha_{opt} \approx 0.77 \, \alpha^{\frac{1}{4}} / C_s^{\frac{1}{4}}$  [83].

Since no concave magnetic lenses exist, the correction for spherical aberration is rather difficult but can be performed using complex arrangements of quadrupoles, hexapoles and/or octupoles, so-called spherical aberration or  $C_s$  correctors [87]. The use of a  $C_s$  corrector allows the use of larger beam limiting apertures, resulting in a decreased influence of the diffraction effect.

Another important aberration is chromatic aberration, described by the coefficient  $C_c$ . The electron source of a TEM does not emit monochromatic electrons. The energy spread depends on the type of electron source and is on the order of 0.7 eV for a Schottky field emitter [83]. Due to the chromatic aberration not all of the electrons are focused in the same image plane by the lenses, resulting in an increased disc diameter of the electron probe on the specimen. One way to circumvent this problem is to use a monochromator which reduces the energy spread in the beam. Since the beam intensity is reduced considerably by a monochromator, this often is not a worthwhile solution. A better solution would be to use lens elements that correct for the effects of chromatic aberration, so-called  $C_c$  correctors. These correctors are not routinely used yet.

#### 3.6.3 Electron beam damage

Damage induced in the specimen by the electron beam often limits the possibilities to investigate specimen properties. The beam damage is caused by inelastic collisions of the electrons with atoms in the specimen. Beam damage can be divided into three categories which will be introduced here. More information about these beam damage mechanisms can be found in reference [83]. Subsequently, measures to reduce the impact of electron beam damage in this work are described.

#### Radiolysis

The incident electrons can break bonds in some materials through ionisation. Most commonly this happens in polymers, where the electrons can either break the main polymer chains and change their structure and properties, or break side groups and create radicals, which can then form new structures through cross-linking.

#### Knock-on damage / sputtering

Knock-on damage describes the effect of displacement of atoms in the specimen due to the transfer of kinetic energy from the incoming electrons. This can happen in crystalline materials and create point defects, but also in unordered structures. Atoms can also be ejected from the specimen surface, this process is called sputtering. Both of these processes occur if the kinetic energy that can be transferred from the electrons to the specimen is higher than the threshold energies for displacement and sputtering, which vary between elements. The maximum kinetic energy that can be transferred depends on the electron energy and is larger for higher energies. With a 300 keV electron beam, sputtering can be induced in many materials [83].

#### Specimen heating

Specimen heating is caused by phonons that are excited by the electron beam. If the specimen is heat sensitive, specimen damage can occur due to the increased temperature. Heating is most relevant for specimens with poor thermal conductivity, like for example polymers and ceramics. The effect of specimen heating is usually reduced if the energy of the electron beam is increased, as this decreases the cross section for inelastic scattering and reduces interaction between the electron beam and the specimen.

#### Low-dose imaging of catalytic NPs

Knock-on damage is especially problematic when imaging NPs in STEM mode. When the detailed atomic structure of the NPs is of interest, as in the work presented in Paper V, knock-on damage needs to be minimised in order to retain and measure the intrinsic NP properties. Since the acceleration voltage of the TEM often cannot be reduced sufficiently without losing too much spatial resolution, the approach used in this work was to reduce the beam current as much as practically possibly. While using a low beam current, the NPs could be imaged for a certain time before any noticeable changes in the structure of the NPs occurred. The electron beam current used in Paper V was around 3 pA and was determined using a calibrated CCD camera. The calibration of the CCD camera was tested by comparing the obtained current values with the 'Screen current' readout of the instrument while using a larger beam current of around 100 pA. During the experiments, this instrument readout could not be used since the beam current was below the measurement threshold.

#### 3.6.4 Instrumentation

The STEM imaging presented in this thesis was performed using an FEI Titan 80- $300^{\text{TM}}$  (S)TEM equipped with a Schottky field-emission source operated at acceleration voltages of 200 and 300 kV. The instrument is fitted with a probe aberration corrector which allows focusing the electron probe to a spot smaller than 0.1 nm in STEM mode. The STEM imaging was performed using a HAADF detector for Z-contrast imaging. Inner / outer collection angles between 43 / 215 mrad and 68 / 340 mrad were used. A diode-type Si EDX detector was used to acquire X-ray spectra for chemical characterisation.

STEM EDX mapping was performed using an FEI Titan  $80-200^{\text{TM}}$  (S)TEM instrument equipped with a Super-X<sup>TM</sup> EDX detector [88] and a probe aberration corrector. Prior to all TEM investigations, the specimens were cleaned in a diluted oxygen plasma to minimise carbon contaminations.

### 3.7 Particle size analysis

Particle sizes were determined from the SEM and STEM images using the procedure illustrated in Figure 3.4: The raw image (Figure 3.4a) was analysed and the NPs were manually identified. The NPs were marked to create a binary image as shown in Figure 3.4b. Using a particle analysis function, all particles in the binary image were detected and their projected areas  $A_p$  were measured. All these steps were performed in the software ImageJ [89]. Assuming spherical shapes of the NPs, a projected area diameter was calculated using:

$$D_p = 2\sqrt{\frac{A_p}{\pi}} \tag{3.9}$$

The diameters were sorted into equally sized bins and plotted as particle size distributions (PSDs), as shown in Figure 3.4c. Data from multiple similar images was combined to obtain a statistically relevant amount of particles.



Figure 3.4: Process of creating PSDs from SEM and TEM images. NPs in the image are manually detected and the image is binarised. The projected area of each particle is measured and projected area diameters are calculated. These are sorted into equally sizes bins and plotted as a PSD.

### 3.8 Non-rigid image registration and strain analysis

In Paper V, high-precision STEM measurements were performed in order to investigate strain in supported NPs. Several factors limit the precision of such measurements. The image precision is here defined as the standard deviation of repeated measurements of distances in an image, for example interatomic spacings. Serial acquisition in STEM mode leads to deformation of the images due to instabilities in the position of the sample and electron probe. Averaging of several frames of an image series can be used to reduce the impact of these instabilities on the image precision, as well as to improve the signal-to-noise ratio (SNR). Before averaging, the frames need to be registered and aligned to one another to correct for sample drift between the frames and distortions. Traditionally, rigid registration was used to align frames in an image series [90]. In rigid registration, the frames are shifted and rotated with respect to each other to find the best fit between them, without deformation of the frames themselves.

In this work, a non-rigid registration (NRR) method was applied that performs a pixelwise deformation to the images to find the best match between consecutive frames of an image series [91, 92]. The NRR was first applied to a downscaled version of the frames and the resulting measured deformations were used as an initial guess for the NRR of the frames with the original resolution. The downscaling was performed to avoid local minima in the matching process. After the NRR, the aligned frames were averaged to create a final image with a high image precision and SNR.

In the resulting averaged image, two-dimensional Gaussian functions were fitted to each atomic column in order to obtain the atomic column positions. In each grain of the NP, a precision area was defined. The precision areas were at least four atomic layers away from any grain boundary, surface or interface, and therefore assumed to be mostly distortion free. The nearest-neighbour distances in three crystallographic directions within the precision areas were then measured. The average nearestneighbour distances were used as reference values for strain measurements and the standard deviations were used as a measure for the image precision.

Two different methods were utilised to visualise NP lattice deformations: Displacement maps and strain maps. To create displacements maps, an ideal periodic lattice was generated in each grain using the average interatomic spacings from the precision areas. The periodic lattice was then extended over all atomic column positions in the NP and represents the structure of the NP if no deformations were present. For the ideal lattice positions at twin boundaries, where each atomic column belongs to two different grains, averaged lattice positions were used. The relative displacements of the measured atomic column positions from their ideal lattice positions were then determined and indicated as arrows in the displacement directions in the STEM images. Displacement maps illustrate lattice deformations in an intuitive way. However, since the ideal periodic lattice is aligned to the precision areas, displacements tend to accumulate the further an atomic columns is away from a precision area. Therefore, the measured displacement of an atomic column cannot be easily interpreted in a quantitative way.

Strain maps are an alternative way to illustrate lattice deformations. The distances of each atomic column to its nearest neighbours in three crystallographic directions were measured. Strain was here defined as the deviation of the measured distances from the average spacing within the precision area divided by the average spacing. Strains in the three crystallographic directions were treated individually. For each direction a strain map was created where the strain values were indicated on a colour scale between each two neighbouring atomic columns. Strain values above and below the extreme values of the colour scale were marked in different colours to highlight large strains. Strains that were within the range of the colour scale were averaged over all nearest neighbour columns to reduce noise in the strain maps.

### 3.9 Energy-dispersive X-ray (EDX) spectroscopy

The interaction of the electron beam with the specimen (in either SEM or TEM) creates characteristic X-ray radiation. The incoming electrons ionise part of the atoms in the specimen, electrons from higher electronic states are transferred to lower energy states and the difference in energy is emitted in the form of X-ray quanta. Additionally, a continuous background spectrum (Bremsstrahlung) is emitted due to electrons being retarded by electrostatic interactions with the nuclei in the material.

An X-ray detector is mounted above the specimen. The most common type is a solid state Si detector consisting of a reverse-biased p-i-n diode ('p-doped'-'intrinsic'-

'n-doped'). An X-ray entering the detector creates a number of electron-hole pairs proportional to its energy. The number of separated charges is counted and the energy of the incident X-ray is calculated. The energy resolution of such an energy-dispersive X-ray detector is quite poor, typically around 140 eV [83].

In many cases, the elements present in the specimen can directly be determined from the X-ray lines identified in the spectrum. To quantify the concentrations of different elements, the following procedure can be applied: First, the continuous background in the spectrum needs to be subtracted. One way to do this is to define background windows in regions without characteristic peaks and then model the background in the remaining regions by polynomial functions or by interpolation. Once the background is subtracted, the intensities of a certain family of X-ray peaks (K, L, M, ...) of an element are integrated. If two elements A and B are present in the specimen and the integrated intensities  $I_A$  and  $I_B$  are measured, the *Cliff-Lorimer* equation allows the calculation of the ratio of the weight percent of each element,  $C_A$  and  $C_B$  [83]:

$$\frac{C_A}{C_B} = k_{AB} \frac{I_A}{I_B} \tag{3.10}$$

 $k_{AB}$  is a sensitivity factor that accounts for the difference between the generated and measured X-ray intensities. It depends mainly on the atomic number Z of the two elements, the absorption of X-rays within the specimen and the fluorescence of X-rays in the specimen. A precise knowledge of this so-called k-factor is crucial for an accurate quantification, but is often hard to obtain. The above mentioned steps can be performed almost automatically in most modern EDX software packages.

Pre-defined k-factors can be used, which is often sufficient to obtain useful information about the specimen, estimate chemical compositions and compare different regions of the specimen. One should keep in mind, though, that for a very precise absolute quantification a more thorough determination of the k-factors is needed, procedures for that are described in reference [83].

Different modes can be used to acquire EDX data. The simplest one is to position the electron beam on one spot of the specimen and acquire a spectrum (spot analysis). Alternatively, the electron beam can be scanned continuously over an area of the specimen while a spectrum is collected. This spectrum will then show the integrated (average) composition of that region. If spatially resolved information is needed, X-ray spectra can be acquired at multiple points of a line (line scan) or at all positions of a two-dimensional spot pattern (mapping). Afterwards, the chemical composition can be evaluated at each position of the respective pattern, resulting in a compositional profile or chemical map of the specimen. In STEM, the HAADF signal can be recorded simultaneously with the X-ray spectra to correlate features in the image with the composition. A problem with EDX mapping is the acquisition time for the large number of X-ray spectra that need to be recorded. Specimen beam damage, specimen drift and / or contamination build-up can limit the possibilities to obtain useful EDX maps. For many materials, the damage induced by the electron beam is the largest challenge and can often only be reduced by using very efficient detection systems that allow shorter acquisition times.

# 3.10 Focused ion beam / scanning electron microscopy (FIB/SEM)

A focused ion beam / scanning electron microscope (FIB/SEM) is an instrument that combines an electron column with optics like in an SEM with an ion column that can form a focused ion beam, often using gallium ions. The same imaging and spectroscopy modes as described in Section 3.5 can be performed using the electron beam, while the ion beam can be used to image the specimen (by detecting secondary electrons which are created upon ion impact) and to sputter away material in a controlled and localised way. The sputter rate of the ion beam can be controlled by the ion energy and current. In most instruments, the electron and ion beams are tilted  $52^{\circ}$  with respect to each other and the specimen is placed in the coincidence point of the two beams as illustrated in Figure 3.5. The specimen is usually facing the ion beam during ion milling. The electron beam can be used to image the progress of the milling. Additionally, metals (often mixed with carbon) can be locally grown on the specimen by introduction of a metal-containing gas into the chamber. The electron or ion beam interacts with the gas, resulting in local deposition of a metal-containing layer. Even other materials like carbon can be deposited. This is routinely used to weld a micromanipulator to the specimen or to attach slices that were extracted from a sample to a TEM grid.

#### 3.10.1 FIB/SEM TEM specimen preparation

The FIB/SEM was used to prepare thin foil specimens for TEM investigations. Two trenches were milled into the surface of a specimen using the ion beam, leaving a lamella in between those trenches. A micromanipulator was inserted, brought in contact with the lamella and attached by platinum deposition. The lamella was afterwards cut free from the surface, lifted out and attached to a TEM copper grid. Subsequently, the lamella was thinned down further using the ion beam until it had a suitable thickness for TEM investigation. More information about the lift-out technique can be found in references [93,94].

An FEI Versa 3D DualBeam<sup>TM</sup> FIB/SEM was used for the TEM specimen preparation. For imaging of the specimens, an electron beam acceleration voltage of 2 kV was used, while 30 kV was used for the gallium ions. The ion currents ranged from



Figure 3.5: Schematic drawing of the principal setup of a FIB/SEM during ion milling. The specimen surface is usually facing the ion beam. An SE detector is being used to detect SEs created by the electron beam or the ion beam.

 $4.5\,\mathrm{nA}$  for milling of the initial trenches down to about  $40\,\mathrm{pA}$  for the final thinning of the lamellae.

#### 3.10.2 FIB/SEM slice & view tomography

The FIB/SEM was also used for three-dimensional imaging of catalyst specimens by applying so-called slice & view tomography. The surface of the specimen was imaged using the electron beam and a BE detector. Subsequently, a thin layer of the surface was removed by ion beam sputtering and the exposed area was imaged. This procedure was repeated until a certain volume of the specimen was removed and a stack of images representing that volume was recorded. Using a reconstruction software (FEI Avizo<sup>TM</sup>), a three-dimensional model of that volume was created from the images. For the slice & view experiments, an FEI Helios NanoLab<sup>TM</sup> FIB/SEM was used.

## 3.11 Kinetic Monte Carlo simulations

Kinetic Monte Carlo simulations [95, 96] that rely on scaling relations were used in combination with DFT calculations [97, 98] to asses the impact of strain on catalytic activity. For this purpose, the catalytic activity of supported Pt NPs for CO oxidation was simulated at different temperatures and the contributions of different active sites like corners, edges and facets were determined. Different strain patterns were then introduced into the NP by means of variation of the adsorption energies of CO and  $O_2$  on the active sites. Consequently, the simulations were repeated and the overall catalytic activity as well as the contributions from the individual sites were compared to the unstrained NP.

## 4 Summary of results and discussion

This chapter summarises the main results of this thesis. The first section discusses our experimental approaches to obtain three-dimensional information about the spatial variation in the distribution of catalytic NPs on a support material. The following sections concern the studies we performed to examine different aspects of NP sintering, namely the influence of thermal ageing on a catalyst's structure and its catalytic activity, the effect of the gas composition during thermal ageing on NP sintering, and the effect of a controlled structural inhomogeneity of the support on NP sintering. The last section shows results of our study on strain in supported NPs on different support materials alongside kinetic simulations that demonstrate the impact of this strain on the catalytic activity. The scope of this chapter is not to provide a full representation of all experimental details and results. Instead, a short overview is given to present the advances in high spatial resolution characterisation and the main scientific conclusions. The full details can be found in the appended papers which are cited in the respective sections.

# 4.1 Three-dimensional catalyst structure and distribution of nanoparticles

In this work we explored the three-dimensional structure of a mesoporous  $Pt-Pd/Al_2O_3$  catalyst and the spatial distribution of the metal NPs within the support. The complete experimental details and results are presented in Paper II and Paper IV. Characterisation on a large scale was performed by three-dimensional FIB/SEM slice & view tomography, while characterisation with high spatial resolution relied on HAADF STEM imaging of cross-sectional specimens that were prepared using site specific extraction.

We developed a specimen preparation technique based on FIB/SEM lift-out technology to prepare cross-sectional TEM specimens. Figure 4.1 shows the main steps of the specimen preparation. The alumina support particles that contained the Pt-Pd NPs were nearly spherical with diameters of several micrometres (Figure 4.1a). As a first step, the catalyst powder was embedded in acrylic resin which was then hardened by heat treatment. The hardened block was then cut and polished, which exposed the interiors of some alumina particles as is schematically shown in Figure 4.1b. The gray region depicts the resin, the orange region the alumina support



Figure 4.1: Illustration of TEM specimen preparation by FIB/SEM lift-out. a) SEM image of a Pt-Pd/Al<sub>2</sub>O<sub>3</sub> catalyst support particle attached to an aluminum stub. b) Model of the catalyst support particle embedded in a block of resin and mechanically polished on the top side. c) Top-view SEM image of an embedded and polished Pt-Pd/Al<sub>2</sub>O<sub>3</sub> catalyst. The white rectangle marks a typical region chosen for a lift-out, the red dotted rectangles mark regions for ion beam milling. d) SEM image of the two trenches milled into the surface using the ion beam. e) Side-view SEM image of an extracted slice. Bright regions correspond to alumina, dark regions to embedding resin. Regions from the interior as well as the lower edge of the support particle are preserved. f) Model of the catalyst support particle in cross-sectional view. Point A lies on the outer edge of the support particle, whereas point B lies in the interior of the original support particle. Figure from reference [99] (Paper II).

particle. The surface was coated with a thin carbon film prior to imaging and ion beam milling in order to increase the electrical conductivity. Figure 4.1c shows a top-view SEM image of the polished surface, where an alumina support particle can be seen in the center. Material was removed in the regions marked with red rectangles using a gallium ion beam, the resulting trenches can be seen in Figure 4.1d.

No protective layer was deposited onto the surface before milling in order to prevent contamination of the specimen with metallic NPs during later stages of the preparation. A micromanipulator was attached to the exposed slice and it was cut loose from the surface by the ion beam. Figure 4.1e shows the slice after the liftout, the bright region is a slice of the alumina particle, the dark region the resin. Subsequently the slice was thinned down further using the ion beam. The resulting specimens had a structure similar to the schematic shown in Figure 4.1f. They were slices from the centre of the alumina particles, and the outer edge of the particles on the lower side was intact. This allowed the individual analysis of regions right at the outer edge of the support particles (Point A) and regions from the interior of the support (Point B).

Figure 4.2 shows STEM images of a catalyst specimen obtained by the lift-out method. The center image shows an overview of the extracted region, at the bottom the outer edge of the alumina towards the resin can be seen. The left and right STEM images show the interior region of the support and the near-edge region, respectively. We classified the observed Pt-Pd NPs in three categories and marked some examples: Small NPs (red circles, d < 1.5 nm), medium-sized NPs (green circles,  $1.5 \text{ nm} \leq d \leq 10 \text{ nm}$ ) and large NPs (blue circles, d > 10 nm). We observed that the medium-sized and large NPs were confined close to the outer edge of the support, while the small NPs were evenly distributed over the whole support. We quantified the NP size distributions for the different regions independently and followed the NP sintering caused by thermal ageing locally in those regions (see Section 4.2).

The advantages of the developed TEM specimen preparation method are twofold: Firstly, the cross-sectional view of the specimen makes it possible to obtain threedimensional information about the distribution of NPs within the support material. In our case, it enabled us to observe the confinement of the larger NPs in this sample to the outer edge of the support material. Three-dimensional high spatial resolution structural information on the nanoscale could earlier only be obtained by TEM/STEM tomography. The observable sample volumes with this technique are, however, much smaller compared to the micrometre-sized regions we are able to investigate with our cross-sectional approach.

Secondly, the specimen preparation simplifies the acquisition of quantitative data about the catalyst sample, as for example NP size distributions. The reason is that the structure of the TEM specimen is much more homogeneous compared to other specimen preparation techniques. The most commonly applied technique involves crushing the catalyst powder in a mortar and dispersing the fragments onto a carbon film. While using this technique, we frequently observed fragments containing large



Figure 4.2: Cross-sectional HAADF STEM images of a catalyst sample prepared by the FIB/SEM lift-out method. The central image shows low-magnification overview, the left image shows a region in the interior of the alumina support at higher magnification, while the right image shows a region at the outer edge. The edge of the alumina support is marked by a white dotted line. The Pt-Pd NPs have bright contrast. The inset shows a medium-sized NP at high resolution. In the images at higher magnification, the porous alumina structure can be seen in the background. Some Pt-Pd NPs are highlighted by circles (red: small NPs, green: medium-sized NPs, blue: large NPs). The orange dotted line marks the inner boundary of an outer layer with an increased density of medium-sized and large NPs. Figure from reference [1] (Paper IV).

NPs. Based on those results it was unclear that the large NPs were only present in the outer layer of the support, which only constituted a very small fraction of the total volume of the catalyst particles. The observations therefore conveyed a false impression of the overall size distribution of the NPs in the catalyst. When applying the lift-out preparation technique, we learned that the vast majority of the catalyst volume did not contain any large NPs and was instead homogeneously covered by small NPs below 1.5 nm in diameter. Quantitative size distributions of these small NPs could be obtained by imaging several randomly selected regions within the interior of the support particle.

To investigate the three-dimensional distribution of large NPs within the support with better statistics on an even larger scale, we also performed FIB/SEM slice & view tomography (see Section 3.10.2). With this technique it was possible to obtain three-dimensional positions of the Pt-Pd NPs in the support over large volumes of the specimen, potentially extending over dozens of micrometres in certain directions. Figure 4.3a shows the reconstructed image of one of the investigated catalyst samples. Light blue represents the alumina support, dark blue the Pt-Pd NPs. The measurements confirmed what we had observed in the STEM images, the large NPs were confined to the outer edge of the alumina support particle. Since a much larger number of large NPs was observed with this technique, it also allowed us to obtain more quantitative information. Figure 4.3b shows a histogram of distances from the NPs to the edge of the alumina support. It is clear that most large NPs were within 100 nm to the outer edge, and the average distance to the edge was determined to 36 nm. The FIB/SEM slice & view tomography technique is a useful complementary technique, and its considerably better statistics are advantageous when larger NPs are the focus of interest.



Figure 4.3: Results of FIB/SEM slice & view tomography of a Pt-Pd/Al<sub>2</sub>O<sub>3</sub> catalyst. a) Slice of a three-dimensional reconstruction showing Pt–Pd NPs distributed within an alumina support particle with a diameter of approximately 7 µm. NPs larger than 10 nm could be observed using this technique. The NPs were mainly distributed along the outer edge of the alumina support, only very few were found in the interior region of the support. b) Distribution of distances from the NPs to the edge of the alumina support. Figures from reference [1] (Paper IV).

# 4.2 The effect of thermal ageing on nanoparticle sintering and catalytic activity

Building upon the three-dimensional characterisation techniques introduced in the previous section, we studied the development of NP sizes and spatial distribution during ageing at 500-800 °C. The full description of this work can be found in Paper IV. Representative cross-sectional STEM images of Pt-Pd/Al<sub>2</sub>O<sub>3</sub> catalyst specimens after ageing at different temperatures are shown in Figure 4.4. The center column contains low-magnification overview images of the extracted slices, the left column shows higher-magnification images of regions in the interior of the alumina support

particles and the right column shows higher-magnification images from areas at the outer edge of the support.

We observed that sintering (and thereby disappearance) of the medium-sized NPs occurred first, after ageing at 600 °C, while the small NPs were stable at this temperature. Possible explanations for the effect on the medium-sized NPs are the high density of these particles, as well as their position near the outer edge of the support, where the pore structure of the alumina might be less effective in separating the NPs. After ageing at 700 °C, most of the small NPs had vanished and large NPs had formed even in the interior region of the alumina support (Figure 4.4d). Ageing at a higher temperature of 800 °C further slightly increased the average size of the large NPs and led to the formation of a considerable amount of NPs with diameter above 50 nm in diameter, which were scarce at lower temperatures. The investigation of the large NPs was assisted by SEM measurements since the larger NP size enabled them to be imaged by SEM.

FIB/SEM slice & view tomography was performed on the catalyst sample aged at 800 °C. A reconstructed image as well as a histogram of distances of the NPs to the edge of the alumina support are shown in Figure 4.5 (results from the untreated catalyst are shown in Figure 4.3). These measurements established an even distribution of large NPs over the whole support particle after heat treatment, except for the very outer edge which still had a higher number density. Combined with the even distribution of small NPs observed before the heat treatment by STEM imaging, we concluded that the sintering occurred on a relatively local scale, and no major net transfer of platinum over the support took place.

We also investigated the impact of the observed NP sintering on the catalytic activity for CO oxidation at low temperatures (Figure 4.6). The results show that the activity decreased moderately after ageing at 500 and 600 °C, although we did not observe any severe NP sintering at those temperatures. However, our measurements also revealed individual Pt and Pd atoms, as well as small clusters on the support surface. Although we could show their presence, it was not possible to reliably quantify them. Sintering of these individual atoms and small clusters is a possible explanation for the decline in catalytic activity already after ageing at low temperatures.

A strong decrease in activity was observed after ageing at 700 and 800 °C. These are the ageing temperatures at which we had observed severe sintering of small NPs and the formation of large NPs all over the alumina support. We could also extract the apparent activation energies of the catalysed CO oxidation reaction from the conversion graphs and show that the apparent activation energy increased with increasing ageing temperature. The measurements highlight the importance of small NPs for the activity for CO oxidation of this Pt-Pd/Al<sub>2</sub>O<sub>3</sub> catalyst.



**Figure 4.4:** STEM images of the fresh and aged catalyst prepared by the FIB/SEM lift-out method. The central column shows low-magnification overview images, the left column shows images at higher magnification from regions in the interior of the alumina support, while the right column shows regions at the outer edge. The inset in subfigure a) shows a medium-sized NP at high resolution. The edge of the alumina support is marked by a white dotted line. Some Pt-Pd NPs are highlighted by circles (red: small NPs, green: medium-sized NPs, blue: large NPs). Figure from reference [1] (Paper IV).



**Figure 4.5:** Results of FIB/SEM slice & view tomography of a Pt-Pd/Al<sub>2</sub>O<sub>3</sub> catalyst aged at 800 °C. a) Slice of a three-dimensional reconstruction showing Pt-Pd NPs distributed within an alumina support particle with a diameter of around 15 µm. The Pt-Pd NPs were evenly distributed within the alumina support except for a high number density very close to the outer edge. The NPs are color-coded by their distance to the alumina edge from blue (close to the edge) to red (far from the edge). b) Histogram showing the distribution of distances from the NPs to the edge of the alumina support. Figures from reference [1] (Paper IV).

# 4.3 The effect of gas composition on nanoparticle sintering and catalytic activity

We studied the effect of the gas composition during thermal ageing of a  $Pt/Al_2O_3$  catalyst. The dispersion (number of Pt surface atoms relative to total number of Pt atoms) and NO oxidation activity of the catalyst were evaluated after ageing under different conditions. The dispersion was measured by CO adsorption and the NO oxidation activity was determined in a continous-flow reactor. The full experimental details and results are presented in Paper I. Thermal ageing was performed at different temperatures (600-900 °C) in atmospheres of Ar, O<sub>2</sub>, H<sub>2</sub>, SO<sub>2</sub> and SO<sub>2</sub> + O<sub>2</sub> for 2 hours. The general trend that was observed after ageing in the inert Ar atmosphere was a decrease in the Pt dispersion (Pt NP growth) with increasing temperature, accompanied by an increase in NO oxidation activity. It should be noted that the NO oxidation reaction, in contrast to CO oxidation which was used as a model reaction in the other parts of this work, has been shown to benefit from larger Pt NPs [100, 101].

The presence of  $O_2$  and/or  $SO_2$  during the ageing had the most striking impact as is shown in Figure 4.7. All measurements at 500 °C were taken after a degreening procedure in identical atmospheres, at 600 °C the respective ageing atmospheres were introduced. Figure 4.7a shows that the presence of  $O_2$  led to an increase in NO oxidation activity (or conversion) at temperatures of 600-700 °C compared to the Ar atmosphere, while the activity slightly droped at 800-900 °C. At the



Figure 4.6: Activity for CO oxidation of the fresh and aged catalyst samples. The conversion measurements were performed in a continuous-flow reactor during a cooling ramp in 4% O<sub>2</sub> and 1000 ppm CO balanced with argon. Figure from reference [1] (Paper IV).

highest temperatures, the Pt dispersion was strongly decreased in the presence of  $O_2$ . The facilitating role of  $O_2$  on NP sintering and decrease in dispersion is commonly explained by the formation of volatile compounds and PtO species that have a higher mobility on the support material compared to metallic platinum [102].

Figure 4.7b shows the Pt dispersion and NO oxidation activity after ageing in  $SO_2$  and  $SO_2 + O_2$ . In both cases, the initial thermal ageing at 600 °C drastically decreased the Pt dispersion, while only the sample aged in  $SO_2 + O_2$  gained a considerably higher activity compared to the Ar sample. At the higher temperatures, the sample aged in  $SO_2$  retained a relatively high dispersion, while ageing in  $SO_2 + O_2$  led to an extremely low dispersion. As was the case for the sample aged in  $O_2$ , the  $SO_2 + O_2$  atmosphere resulted in a slight loss in activity at the highest ageing temperatures. The apparent increase in dispersion after ageing at 800 °C in  $SO_2$  was likely not due to redispersion, but due to residual sulphur on the sample surface after ageing at the lower temperatures, for more details see Paper I.

These results indicate that  $O_2$  strongly promotes Pt NP sintering at high temperatures, while SO<sub>2</sub> promotes sintering at relatively low temperatures (which 600 °C is in terms of thermal ageing). It should be noted that the strong measured decrease in dispersion under the presence of SO<sub>2</sub> could also partly be caused by sulphur deposition on the samples instead of NP sintering, but it was shown that this would only account for a small fraction of the total decrease.

To further evaluate the effect of SO<sub>2</sub> at low temperatures, ageing at 250 °C in an SO<sub>2</sub> + O<sub>2</sub> atmosphere was performed for 22 hours. CO adsorption showed that the dispersion decreased from 65% to 25%, which is a strong decrease considering the



Figure 4.7: Pt dispersion and NO conversion for different thermal ageing atmospheres versus ageing temperature. The NO conversion represents the NO oxidation activity. Catalyst samples at 500 °C were all subjected to the same degreening procedure, at 600 °C the respective ageing atmospheres were introduced. a) Results for catalyst samples aged in Ar and 10% O<sub>2</sub> in Ar. b) Results for catalyst samples aged in 30 ppm SO<sub>2</sub> + 10% O<sub>2</sub> in Ar. Both figures from reference [103] (Paper I).

low ageing temperature. To verify that NP sintering occurred, STEM imaging was performed on the fresh and aged samples. The results (Figure 4.8) show that the fresh catalyst samples only contained small Pt NPs with diameters around 1 nm, while after ageing at 250 °C in  $SO_2 + O_2$  a mixture of NP sizes between 1 nm and around 40 nm were present.



**Figure 4.8:** HAADF STEM images of the fresh catalyst (a and b) and after ageing at  $250 \,^{\circ}$ C in SO<sub>2</sub> + O<sub>2</sub> for 22 h (c and d). While the fresh catalyst only contains small NPs around 1 nm in diameter, the low-temperature aged catalyst contains a wide range of particle sizes between 1 nm and around 40 nm. All figures from reference [103] (Paper I).

The NO oxidation activity of the catalyst after the low-temperature ageing was comparable to the catalyst aged in  $SO_2 + O_2$  at 700 °C (but for a shorter time). The dispersion of the low-temperature aged catalyst was considerably higher though, which means that the dispersion is not the only factor influencing the catalytic activity. We suggested that the presence of sulphur could increase the acidity of the alumina support, which has been observed before for a zirconia support [104]. A more acidic support would suppress platinum oxide formation and thereby increase the activity of the catalyst for NO oxidation. A low-temperature treatment in an atmosphere containing  $SO_2$  and  $O_2$  can be a viable way of increasing the NO oxidation activity of a catalyst without causing too much NP growth. This could be beneficial since NP growth is detrimental for most other reaction which the catalyst also has to perform.

### 4.4 The effect of support nanostructure on sintering and redispersion of platinum nanoparticles

We studied the effect of controlled structural heterogeneity of the support material on the sintering and redispersion behaviour of Pt NPs. The full work is presented in Paper III. The study was performed on a model support material consisting of a flat  $Si_3N_4$  membrane covered by a thin sputter-coated alumina layer. Additionally, the surface was decorated with nanofabricated alumina cones (diameter at base of around 80 nm), which were also covered by a sputter-coated alumina layer. On this support, Pt NPs were deposited by e-beam evaporation and subsequent heating. Figure 4.9 shows a sketch as well as TEM/STEM images of the resulting structure.



Figure 4.9: a) Schematic illustration of Pt NPs supported on a nanostructured alumina surface on a TEM membrane. b) TEM image of an array of nanofabricated alumina cones on a flat surface, both homogeneously sputter-coated by a 10 nm thick amorphous alumina layer to ensure chemical homogeneity. c) STEM image of a single nanocone and the adjacent flat area decorated with Pt NPs. Note the clear difference in Pt particle size and density on the cone and on the flat area, respectively. Figure from reference [105] (Paper III).

Samples were thermally aged at 600 °C in an atmosphere of 4%  $O_2$  in Ar for 4, 10, 30 and 60 minutes. For each ageing time, STEM imaging was performed in order to obtain NP size distributions on the flat part of the support as well as on the nanocones. Even before thermal ageing, different NP sizes and distributions were observed in these two areas. Initially, a smaller average NP size and higher NP density was observed on the cones. With progressing ageing, the NP distributions in the two areas also developed differently.

On the flat part of the support, some NPs grew in size while others decreased in size, resulting in a bimodal NP size distribution. This was interpreted as a result of the Ostwald ripening mechanism, where individual atoms migrate from smaller to larger NPs. On the cone surfaces, almost all NPs drastically decreased in size, and after 60 minutes almost only small NPs below 2 nm in diameter remained. The analysis showed that the particle density on the cones strongly increased during the ageing procedure, while the surface coverage strongly declined. The remaining small NPs on the cones appeared to be much more stable compared to the ones on the flat part of the support. Figure 4.10 shows a series of STEM images that illustrates the development in the two different areas.



Figure 4.10: Representative HAADF STEM images of Pt NPs on the flat part of the support and on the nanofabricated cones after different ageing durations. On the flat area, growth of some NPs and shrinkage of others were observed. On the cones, strong redispersion was seen and almost only small NPs remained after 60 minutes of thermal ageing. Figure from reference [105] (Paper III).

The overall removal of Pt from the cone surfaces can be explained by the initial smaller NP sizes. When Ostwald ripening is occurring, there is a transport of material from smaller NPs to larger ones, which in this case were situated on the flat parts of the support. Also, the initial small NPs on the cones have an inherently lower stability compared to larger ones. A striking observation was the high thermal stability of the remaining small NPs on the cones after 60 minutes of ageing. We suggested that this stability could be explained by anchoring of these NPs on defect sites on the alumina surface. If there was an abundance of defect sites on the nanofabricated cones, this could explain both the redispersion on the cones (the defect sites "catch" diffusing Pt atoms), as well as the high stability of the resulting small NPs.

In order to identify possible defect sites on the cones, TEM imaging was performed (Figure 4.11). The top-view TEM image in Figure 4.11a suggests that the surface of the cone is not smooth since a steplike corrugation can be seen. Even the side-view TEM images in Figure 4.11b and c suggest a wavy and partly steplike shape of the cone wall. These observed features are likely anchoring sites for small NPs and contribute to the observed redispersion and stability of small NPs.

This work demonstrates how a controlled structural heterogeneity in an otherwise simple model system can help to obtain a better understanding of phenomena that were earlier observed on more complex mesoporous catalysts, like redispersion and bimodal size distributions, but not sufficiently understood.



**Figure 4.11:** a) Top- and b,c) side-view TEM micrographs of a cone at different magnifications revealing structural irregularities on the cone surface that may act as preferred anchoring sites for the redispersed Pt NPs and provide them with significant sintering resistance due to the site-specific energetics. The blue arrows point to the edge of the cone in subfigure c, the contrast on the left side is from the flat alumina surface in the background. Figure from reference [105] (Paper III).

## 4.5 Determination of strain in supported nanoparticles and the effect on catalytic activity

We studied strain in Pt NPs supported on alumina as well as ceria using highresolution STEM with atomic resolution, extracting information about the positions of the atomic columns with picometre precision. The observed strain patterns served as a starting point for kinetic Monte Carlo simulations to elucidate the impact of the observed strain on the catalytic activity for CO oxidation. The full work can be found in Paper V. The high-resolution STEM images were obtained by averaging tens to hundreds of frames of an image series. Before averaging, corrections for image distortion and drift were performed using a pixel-by-pixel non-rigid registration scheme [92]. To minimise changes in the NPs during the acquisition of the image series, a low electron beam current of around 3 pA was used.

Figure 4.12a shows an averaged side-view STEM image of a Pt NP supported on  $\gamma$ -alumina. The left, right and upper surfaces terminate to vacuum, while the lower part of the image shows an interface between the Pt NP and the alumina support. The alumina support is barely visible in this image due to its weak atomic number contrast in HAADF STEM images. A twin boundary can be seen in the image and is marked by a red rectangle. The image precision was determined to be 2.1 pm.

An atomic column displacement map is shown in Figure 4.12b, strain maps in three crystallographic directions in Figure 4.12e-f and a histogram of strains in Figure 4.12c. Experimental details about the displacement and strain maps can be found in Paper V and Section 3.8. The strain maps show a higher concentration of large strains at the interface between the NP and the alumina support compared to other parts of the NP. This can also be seen in the strain histogram which shows that most strains larger than 5% were found at the interface. We noticed that most of the large interfacial strains were compressive. In the directions perpendicular to the twin boundary, expansive strains of 1-2% were observed close to the boundary.

Figure 4.13 shows additional averaged STEM images, displacement maps and strain maps of (from left to right) a Pt NP supported on ceria (side view), two Pt NPs on alumina (side view) and a Pt NP on alumina (top view). The side-view images show similar trends as was seen in Figure 4.12, particularly a high concentration of large strains at the NP-support interfaces. In Figure 4.13a, the ceria grain is also in a zone axis orientation with its atomic structure resolved.

The interfacial strain can be caused by different mechanisms, for example dislocations at the interface, mismatch in lattice parameters and thermal expansion coefficients, as well as surface corrugation of the support [106]. The observed interfacial strains in the two catalysts may be composed of a combination of different mechanisms. The alumina support had a different morphology compared to the ceria support and did not exhibit extended facets and large, single-crystalline grains. Instead, the surfaces of the alumina grains were mostly corrugated. Despite these



Figure 4.12: a) Average of 148 side-view HAADF STEM images of a Pt NP supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. The lower part of the NP is in contact with the Al<sub>2</sub>O<sub>3</sub> support, the upper part terminates to vacuum. A twin boundary is marked by a red rectangle. b) Displacement map showing the deviation of atomic column positions from an ideal lattice. The arrows indicate the displacement direction, their length and colour coding the magnitude of the displacement. The largest displacements can be observed at the NP-support interface. c) Histograms showing the distribution of strains for the whole NP, as well as for the outermost layer at the free surface of the NP and the interface between the NP and the  $Al_2O_3$  support. d) – f) Strain maps showing deviations of nearest neighbour distances relative to the values within the precision area. The arrows indicate the directions of the measured strains. The crystallographic planes in which the strains were determined are indicated above the NP. The colour scale spans from red (-3.5%, compressive) to blue (3.5%, expansive). Strains above these thresholds are highlighted in yellow (large compressive strains) and turquoise (large expansive strains). Strains that fall within the colour scale range were averaged over all nearest neighbours. The largest strains can be observed at the NP-support interface, while the twin boundary contains smaller but consistent strains perpendicular to the boundary. Figure from Paper V.



**Figure 4.13:** Averaged HAADF STEM images, displacement maps and strain maps of supported NPs. a) Side-view STEM image of a Pt NP supported on ceria. The NP as well as the ceria support are atomically resolved. f,k) Side-view STEM images of Pt NPs supported on alumina. The interfaces between the NPs and the support are at the lower edge of the NPs. p) Top-view STEM image of a Pt NP supported on alumina. Larger versions of these images can be found in the SI of Paper V. Figure from Paper V.

differences, we observed interfacial strain in similar magnitudes and a clear increase of strain at the interfaces compared to other regions of the NPs in both samples. The mechanisms causing interfacial strain are likely relevant in many types of supported NP catalysts.

We performed kinetic Monte Carlo simulations to investigate the impact of the observed strain patterns on the catalytic activity of the NPs. Figure 4.14 shows the turnover frequencies for CO oxidation at 900 K for simulated NPs with strain applied to different sites. We found a considerable variation of the turnover frequencies depending on the different strain patterns, with compressive strain in general being more beneficial than expansive strain. We also investigated the impact of strain on the contribution of different actives sites like edges, corners and different facets. We found that the most beneficial value of strain varies among these different active sites.

Future catalyst design can benefit from knowledge gained by a combination of high-precision measurements and kinetic simulations of the contribution of different active sites and their behaviour under strain. This knowledge can assist in the process of tailoring the interfacial strain of supported NPs with the goal to optimise their catalytic properties.



Figure 4.14: Turnover frequency for CO oxidation of Pt NPs for various strain patterns at 900 K, obtained by kinetic Monte Carlo simulations. Partial pressures: p(CO) = 20 mbar and  $p(O_2) = 10$  mbar. Figure from Paper V.

## 5 Conclusions and outlook

In this thesis, we investigated various nanostructural aspects of supported NPs and established correlations with their catalytic properties. One key aspect in this thesis was NP sintering, which was addressed in several studies. We observed the occurrence of Pt NP sintering at unusually low temperatures ( $250 \,^{\circ}$ C) in the presence of SO<sub>2</sub>, and accelerated sintering at high temperatures ( $800-900 \,^{\circ}$ C) in the presence of O<sub>2</sub>. When fabricating a controlled structural inhomogeneity on a model support, we noticed Pt redispersion and the development of a bimodal NP size distribution as a result of heat treatment. These phenomena have been observed, but have never been conclusively explained before. High-resolution STEM experiments in combination with activity tests demonstrated the strong detrimental effect of sintering of small NPs below 1.5 nm in diameter.

The second key aspect in this thesis was the three-dimensional distribution of NPs within the oxide support. We developed a TEM specimen preparation method for porous catalyst support particles which provides cross-sectional specimens and gives insight into the radial distribution of NPs on the support. This method enabled us to identify an outer layer of the alumina support in a Pt-Pd/Al<sub>2</sub>O<sub>3</sub> catalyst that contained considerably larger NPs compared to the interior regions. We could also follow NP sintering separately in these different regions. In addition, we applied FIB/SEM slice & view tomography to map the distribution of large NPs in the alumina support over large volumes with excellent statistics.

The determination of strain in supported NPs and its impact on the catalytic properties was the third key aspect. Using high-resolution STEM in combination with non-rigid registration and averaging of image series, we determined lattice deformations with a precision of about 2 pm and found a distinct buildup of large strains at the interfaces between Pt NPs and both alumina and ceria support. Kinetic Monte Carlo simulations were performed and revealed the impact of strain on the catalytic activity for various kinds of active sites on NP models. The experimentally observed strain patterns were also used as structural input for the kinetic simulations.

This work has given new insights into the three-dimensional nanoscale structures and ageing behaviours of supported NP catalysts and strengthened the understanding of the relation between the catalysts' structures and their catalytic properties. Furthermore, our experimental approaches and newly developed TEM specimen preparation method can be used in future studies to extract more quantitative structural information than is often done in routine investigations. The detailed knowledge we obtained about strain in catalytic NPs using high-precision measurements in combination with advanced kinetic modelling demonstrates that strain could be used in the future to further tailor catalysts for specific reactions and high activity.

Numerous aspects of NP catalysts remain to be investigated in future studies. An even better understanding of the nanoscale structure of metallic NPs would benefit the prediction and tailoring of their properties. An obvious limitation of the highresolution investigations presented in this thesis is the two-dimensional character of the obtained images, which is an issue with many microscopy techniques. We identified ways to obtain three-dimensional information about the distribution of NPs in the oxide support. These are, however, not suitable to investigate the NPs themselves on the atomic scale in three dimensions.

The most promising techniques for this purpose appear to be atom counting if only the number of atoms in the atomic columns and their average position are needed [107, 108], and electron tomography if the three-dimensional position of each individual atom is required [109]. While the resolution of electron tomography in the past was not sufficient to resolve atomic structures of NPs in three dimensions [110,111], tremendous progress has been made in recent years, enabling atomic-resolution tomography of nanostructures [109, 112–114]. New EDX detector designs even allow for a combination of STEM tomography and EDX analysis of NPs to investigate their chemical composition on the nanoscale in three dimensions [115,116]. These three-dimensional techniques open up possibilities to broaden our knowledge about supported NP catalysts which have before been extensively studied in two dimensions.

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## Bibliography

- [1] T. Nilsson Pingel, S. Fouladvand, M. Heggen, R. E. Dunin-Borkowski, W. Jäger, P. Westenberger, D. Phifer, J. McNeil, M. Skoglundh, H. Grönbeck, and E. Olsson. Three-Dimensional Probing of Catalyst Ageing on Different Length Scales: A Case Study of Changes in Microstructure and Activity for CO Oxidation of a Pt-Pd/Al<sub>2</sub>O<sub>3</sub> Catalyst. *ChemCatChem*, 2017. http://dx.doi.org/10.1002/cctc.201700479.
- [2] M. A. Sánchez, V. A. Mazzieri, J. M. Grau, J. C. Yori, and C. L. Pieck. Catalytic activity of Pt-Re-Pb/Al<sub>2</sub>O<sub>3</sub> naphtha reforming catalysts. *Journal* of Chemical Technology & Biotechnology, 86(9), 1198 – 1204, 2011.
- [3] T. Hou, S. Zhang, Y. Chen, D. Wang, and W. Cai. Hydrogen production from ethanol reforming: Catalysts and reaction mechanism. *Renewable and Sustainable Energy Reviews*, 44, 132 – 148, 2015.
- [4] V. Mazumder, Y. Lee, and S. Sun. Recent Development of Active Nanoparticle Catalysts for Fuel Cell Reactions. Advanced Functional Materials, 20(8), 1224 - 1231, 2010.
- [5] R. M. Heck, R. J. Farrauto, and S. T. Gulati. *Catalytic Air Pollution Control*. Wiley, 2009.
- [6] C. H. Bartholomew. Mechanisms of catalyst deactivation. Applied Catalysis A: General, 212(1-2), 17 - 60, 2001.
- [7] S. J. Tauster, S. C. Fung, R. T. K. Baker, and J. A. Horsley. Strong Interactions in Supported-Metal Catalysts. *Science*, 211, 1121, 1981.
- [8] M. Ozawa, T. Okouchi, and M. Haneda. Three way catalytic activity of thermally degenerated Pt/Al<sub>2</sub>O<sub>3</sub> and Pt/CeO<sub>2</sub>-ZrO<sub>2</sub> modified Al<sub>2</sub>O<sub>3</sub> model catalysts. *Catalysis Today*, 242, Part B, 329 – 337, 2015.
- [9] P. Loof, B. Stenbom, H. Norden, and B. Kasemo. Rapid Sintering in NO of Nanometer-Sized Pt Particles on γ-Al<sub>2</sub>O<sub>3</sub> Observed by CO Temperature-Programmed Desorption and Transmission Electron Microscopy. *Journal of Catalysis*, 144(1), 60 – 76, 1993.

- [10] D. J. Smith, D. White, T. Baird, and J. R. Fryer. The characterisation of a model platinum/alumina catalyst by high-resolution electron microscopy. *Journal of Catalysis*, 81(1), 107 – 118, 1983.
- [11] X. Chen, Y. Cheng, C. Y. Seo, J. W. Schwank, and R. W. McCabe. Aging, re-dispersion, and catalytic oxidation characteristics of model Pd/Al<sub>2</sub>O<sub>3</sub> automotive three-way catalysts. *Applied Catalysis B: Environmental*, 163, 499 – 509, 2015.
- [12] J. Barbier Jr and D. Duprez. Steam effects in three-way catalysis. Applied Catalysis B: Environmental, 4(2–3), 105 – 140, 1994.
- [13] F. Eigenmann, M. Maciejewski, and A. Baiker. Gas adsorption studied by pulse thermal analysis. *Thermochimica Acta*, 359(2), 131 – 141, 2000.
- [14] T. Lear, N. G. Hamilton, and D. Lennon. The application of temperatureprogrammed desorption, adsorption isotherms and temperature-programmed oxidation to investigate the interaction of CO with alumina-supported palladium catalysts. *Catalysis Today*, 126(1–2), 219 – 227, 2007.
- [15] J. Dawody, L. Eurenius, H. Abdulhamid, M. Skoglundh, E. Olsson, and E. Fridell. Platinum dispersion measurements for Pt/BaO/Al<sub>2</sub>O<sub>3</sub> NO<sub>x</sub> storage catalysts. *Applied Catalysis A: General*, 296(2), 157 – 168, 2005.
- [16] C. Karakaya and O. Deutschmann. A simple method for CO chemisorption studies under continuous flow: Adsorption and desorption behavior of Pt/Al<sub>2</sub>O<sub>3</sub> catalysts. *Applied Catalysis A: General*, 445-446, 221 – 230, 2012.
- [17] H. Dropsch and M. Baerns. CO adsorption on supported Pd catalysts studied by adsorption microcalorimetry and temperature programmed desorption. *Applied Catalysis A: General*, 158(1–2), 163 – 183, 1997.
- [18] C. H. Bartholomew and R. J. Farrauto. Catalyst Characterization and Selection in Fundamentals of Industrial Catalytic Processes, Second Edition, pages 118–196. John Wiley & Sons, Inc., Hoboken, NJ, USA, 2005.
- [19] J. W. Niemantsverdriet. Photoemission and Auger Spectroscopy in Spectroscopy in Catalysis: An Introduction, Third Edition, pages 39–83. Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, 2007.
- [20] J. W. Niemantsverdriet. Vibrational Spectroscopy in Spectroscopy in Catalysis: An Introduction, Third Edition, pages 217–249. Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, 2007.
- [21] S. R. Bare and T. Ressler. Chapter 6 Characterization of Catalysts in Reactive Atmospheres by X-ray Absorption Spectroscopy. Advances in Catalysis, 52, 339 – 465, 2009.
- [22] R. Schlögl. Chapter 5 X-ray Diffraction. Advances in Catalysis, 52, 273 338, 2009.
- [23] M.-K. Min, J. Cho, K. Cho, and H. Kim. Particle size and alloying effects of Pt-based alloy catalysts for fuel cell applications. *Electrochimica Acta*, 45(25–26), 4211 – 4217, 2000.
- [24] R. M. Rioux, H. Song, J. D. Hoefelmeyer, P. Yang, and G. A. Somorjai. High-surface-area catalyst design: synthesis, characterization, and reaction studies of platinum nanoparticles in mesoporous SBA-15 silica. *The Journal* of Physical Chemistry B, 109(6), 2192 – 2202, 2004.
- [25] S. Damyanova and J. M. C. Bueno. Effect of CeO<sub>2</sub> loading on the surface and catalytic behaviors of CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-supported Pt catalysts. *Applied Catalysis* A: General, 253(1), 135 – 150, 2003.
- [26] R. Srinivasan and B. H. Davis. X-ray diffraction and electron microscopy studies of platinum-tin-silica catalysts. *Applied Catalysis A: General*, 87(1), 45 – 67, 1992.
- [27] J. M. Thomas and P. A. Midgley. The Merits of Static and Dynamic High-Resolution Electron Microscopy (HREM) for the Study of Solid Catalysts. *ChemCatChem*, 2(7), 783 – 798, 2010.
- [28] J. C. Yang, M. W. Small, R. V. Grieshaber, and R. G. Nuzzo. Recent developments and applications of electron microscopy to heterogeneous catalysis. *Chemical Society Reviews*, 41(24), 8179 – 8194, 2012.
- [29] A. T. DeLaRiva, T. W. Hansen, S. R. Challa, and A. K. Datye. In situ Transmission Electron Microscopy of catalyst sintering. *Journal of Catalysis*, 308, 291 – 305, 2013.
- [30] T. W. Hansen and J. B. Wagner. Catalysts under Controlled Atmospheres in the Transmission Electron Microscope. ACS Catalysis, 4, 1673 – 1685, 2014.
- [31] I. Chorkendorff and J. W. Niemantsverdriet. Concepts of Modern Catalysis and Kinetics. Wiley, 2007.
- [32] P. Munnik, P. E. de Jongh, and K. P. de Jong. Recent Developments in the Synthesis of Supported Catalysts. *Chemical Reviews*, 115(14), 6687 – 6718, 2015.

- [33] J. W. Niemantsverdriet. Temperature-Programmed Techniques in Spectroscopy in Catalysis: An Introduction, Third Edition, pages 11–38. Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, 2007.
- [34] A. P. Seitsonen and H. Over. Intimate interplay of theory and experiments in model catalysis. Surface Science, 603(10), 1717 – 1723, 2009.
- [35] G. A. Somorjai and Y. Li. Major Successes of Theory-and-Experiment-Combined Studies in Surface Chemistry and Heterogeneous Catalysis. *Topics* in Catalysis, 53(5), 311 – 325, 2010.
- [36] Z. W. Seh, J. Kibsgaard, C. F. Dickens, I. Chorkendorff, J. K. Nørskov, and T. F. Jaramillo. Combining theory and experiment in electrocatalysis: Insights into materials design. *Science*, 355(6321), eaad4998, 2017.
- [37] T. Lv, Y. Wang, S. Choi, M. Chi, J. Tao, L. Pan, C. Z. Huang, Y. Zhu, and Y. Xia. Controlled Synthesis of Nanosized Palladium icosahedra and Their Catalytic Activity towards Formic-Acid Oxidation. *ChemSusChem*, 6(10), 1923 – 1930, 2013.
- [38] C. Cui, L. Gan, M. Neumann, M. Heggen, B. Roldan Cuenya, and P. Strasser. Carbon Monoxide-Assisted Size Confinement of Bimetallic Alloy Nanoparticles. Journal of the American Chemical Society, 136(13), 4813 – 4816, 2014.
- [39] G. J. Leong, M. C. Schulze, M. B. Strand, D. Maloney, S. L. Frisco, H. N. Dinh, B. Pivovar, and R. M. Richards. Shape-directed platinum nanoparticle synthesis: nanoscale design of novel catalysts. *Applied Organometallic Chemistry*, 28(1), 1 – 17, 2014.
- [40] S. Vajda and M. G. White. Catalysis Applications of Size-Selected Cluster Deposition. ACS Catalysis, 5(12), 7152 – 7176, 2015.
- [41] H.-J. Freund, G. Meijer, M. Scheffler, R. Schlögl, and M. Wolf. CO Oxidation as a Prototypical Reaction for Heterogeneous Processes. *Angewandte Chemie International Edition*, 50(43), 10064 – 10094, 2011.
- [42] Y. Zhou, Z. Wang, and C. Liu. Perspective on CO oxidation over Pd-based catalysts. *Catalysis Science & Technology*, 5(1), 69 – 81, 2015.
- [43] J. Lin, X. Wang, and T. Zhang. Recent progress in CO oxidation over Ptgroup-metal catalysts at low temperatures. *Chinese Journal of Catalysis*, 37(11), 1805 – 1813, 2016.
- [44] M. A. Centeno, T. R. Reina, S. Ivanova, O. H. Laguna, and J. A. Odriozola. Au/CeO2 catalysts: Structure and CO oxidation activity. *Catalysts*, 6(10), 158, 2016.

- [45] Y. Zhang, R. W. Cattrall, I. D. McKelvie, and S. D. Kolev. Gold, an alternative to platinum group metals in automobile catalytic converters. *Gold Bulletin*, 44(3), 145, 2011.
- [46] Euro 5 / Euro 6 emission regulations. http://eur-lex.europa.eu/legalcontent/EN/ALL/?uri=CELEX:32007R0715. Accessed: 2017-07-04.
- [47] A. Russell and W. S. Epling. Diesel Oxidation Catalysts. Catalysis Reviews, 53(4), 337 – 423, 2011.
- [48] A. Bellare, D. B. Dadyburjor, and M. J. Kelley. Evolution of bimodal distributions in the sintering of model supported metal catalysts. *Journal of Catalysis*, 117(1), 78 – 90, 1989.
- [49] T. W. Hansen, A. T. DeLaRiva, S. R. Challa, and A. K. Datye. Sintering of Catalytic Nanoparticles: Particle Migration or Ostwald Ripening? Accounts of Chemical Research, 46(8), 1720 – 1730, 2013.
- [50] S. B. Simonsen, I. Chorkendorff, S. Dahl, M. Skoglundh, J. Sehested, and S. Helveg. Direct Observations of Oxygen-induced Platinum Nanoparticle Ripening Studied by In Situ TEM. *Journal of the American Chemical Society*, 132(23), 7968 – 7975, 2010.
- [51] R. J. Liu, P. A. Crozier, C. M. Smith, D. A. Hucul, J. Blackson, and G. Salaita. In situ electron microscopy studies of the sintering of palladium nanoparticles on alumina during catalyst regeneration processes. *Microscopy and Microanalysis*, 10(1), 77 – 85, 2004.
- [52] A. K. Datye, Q. Xu, K. C. Kharas, and J. M. McCarty. Particle size distributions in heterogeneous catalysts: What do they tell us about the sintering mechanism? *Catalysis Today*, 111(1-2), 59 – 67, 2006.
- [53] G. Liu and P.-X. Gao. A review of  $NO_x$  storage/reduction catalysts: mechanism, materials and degradation studies. *Catalysis Science & Technology*, 1(4), 552, 2011.
- [54] N. Takahashi and H. Imagawa. Improvement of Catalysts for  $NO_x$  Storage and Reduction for Gasoline-fueled Automotive Exhaust. Journal of the Japan Petroleum Institute, 52(3), 90 – 101, 2009.
- [55] C. D. Falk and J. J. Mooney. Three-Way Conversion Catalysts: Effect of Closed-Loop Feed-Back Control and Other Parameters on Catalyst Efficiency, 1980. SAE International.
- [56] J. P. Brunelle. Preparation of catalysts by metallic complex adsorption on mineral oxides. *Pure and Applied Chemistry*, 50(9-10), 1211, 1978.

- [57] 50by50 global fuel economy initiative. https://www.fiafoundation.org/ media/46127/50by50-report-2009-lr.pdf. Accessed: 2017-07-04.
- [58] ICCT European vehicle market statistics. http://www.theicct.org/ sites/default/files/publications/ICCT\_Pocketbook\_2016.pdf. Accessed: 2017-07-05.
- [59] European Automobile Manufacturers Association. http://www.acea.be/ statistics/tag/category/share-of-diesel-in-new-passenger-cars. Accessed: 2017-07-05.
- [60] Forbes. https://www.forbes.com/sites/bertelschmitt/2016/10/13/ineurope-diesel-falls-slowly-out-of-favor/. Accessed: 2017-07-05.
- [61] JATO Dynamics. www.jato.com/wp-content/uploads/2017/05/April-2017-Europe-Reg-Release-Final.pdf. Accessed: 2017-07-05.
- [62] ICCT. http://www.theicct.org/news/press-release-vehicle-testsshow-dramatic-variation-nox-emissions-modern-diesel-cars-neweu. Accessed: 2017-07-05.
- [63] ICCT. http://theicct.org/sites/default/files/publications/ICCT\_ NOx-control-tech\_revised%2009152015.pdf. Accessed: 2017-07-05.
- [64] Forbes. https://www.forbes.com/sites/michaeltaylor/2017/07/18/ daimler-gets-strong-armed-by-germany-over-its-dirty-dieselsrecalls-3-million-cars/. Accessed: 2017-08-17.
- [65] Forbes. https://www.forbes.com/sites/bertelschmitt/2017/08/03/ after-the-diesel-summit-germany-at-a-loss/. Accessed: 2017-08-17.
- [66] A. Chaloulakou, I. Mavroidis, and I. Gavriil. Compliance with the annual NO<sub>2</sub> air quality standard in Athens. Required NO<sub>x</sub> levels and expected health implications. Atmospheric Environment, 42(3), 454 465, 2008.
- [67] D. L. Mauzerall, B. Sultan, N. Kim, and D. F. Bradford.  $NO_x$  emissions from large point sources: variability in ozone production, resulting health damages and economic costs. *Atmospheric Environment*, 39(16), 2851 2866, 2005.
- [68] Euro 1 emission regulation. http://eur-lex.europa.eu/legal-content/ EN/ALL/?uri=CELEX:31991L0441. Accessed: 2017-07-04.
- [69] Euro 2 emission regulation. http://eur-lex.europa.eu/legal-content/ EN/ALL/?uri=CELEX:32002L0051. Accessed: 2017-07-04.

- [70] Euro 3 / Euro 4 emission regulations. http://eur-lex.europa.eu/legalcontent/EN/ALL/?uri=CELEX:31998L0069. Accessed: 2017-07-04.
- [71] N. Takahashi, H. Shinjoh, T. Iijima, T. Suzuki, K. Yamazaki, K. Yokota, H. Suzuki, N. Miyoshi, S. Matsumoto, T. Tanizawa, T. Tanaka, S. Tateishi, and K. Kasahara. The new concept 3-way catalyst for automotive lean-burn engine:  $NO_x$  storage and reduction catalyst. *Catalysis Today*, 27(1–2), 63–69, 1996.
- [72] S. Roy and A. Baiker.  $NO_x$  storage-reduction catalysis: from mechanism and materials properties to storage-reduction performance. *Chemical Reviews*, 109(9), 4054 91, 2009.
- [73] A. Morlang, U. Neuhausen, K. V. Klementiev, F. W. Schütze, G. Miehe, H. Fuess, and E. S. Lox. Bimetallic Pt/Pd diesel oxidation catalysts: Structural characterisation and catalytic behaviour. *Applied Catalysis B: Environmental*, 60(3-4), 191 – 199, 2005.
- [74] O. K. Ezekoye, A. R. Drews, H. W. Jen, R. J. Kudla, R. W. McCabe, M. Sharma, J. Y. Howe, L. F. Allard, G. W. Graham, and X. Q. Pan. Characterization of alumina-supported Pt and Pt–Pd NO oxidation catalysts with advanced electron microscopy. *Journal of Catalysis*, 280(1), 125 – 136, 2011.
- [75] G. W. Graham, H. W. Jen, O. Ezekoye, R. J. Kudla, W. Chun, X. Q. Pan, and R. W. McCabe. Effect of alloy composition on dispersion stability and catalytic activity for NO oxidation over alumina-supported Pt–Pd catalysts. *Catalysis Letters*, 116(1-2), 1 – 8, 2007.
- [76] K. Kallinen, A. Moreno, A. Savimäki, and T. J. J. Kinnunen. Pt/Pd Diesel Oxidation Catalyst : A Study on the Properties Enhanced by the Use of Pd, 2009. SAE Technical Paper 2009-26-0018.
- [77] C. H. Kim, M. Schmid, S. J. Schmieg, J. Tan, and W. Li. The Effect of Pt-Pd Ratio on Oxidation Catalysts Under Simulated Diesel Exhaust, 2011. SAE Technical Paper 2011-01-1134.
- [78] T. R. Johns, J. R. Gaudet, E. J. Peterson, J. T. Miller, E. A. Stach, C. H. Kim, M. P. Balogh, and A. K. Datye. Microstructure of Bimetallic Pt-Pd Catalysts under Oxidizing Conditions. *ChemCatChem*, 5(9), 2636 2645, 2013.
- [79] M. Sato, T. Kanbayashi, N. Kobayashi, and Y. Shima. Hydroxyl groups on silica, alumina, and silica-alumina catalysts. *Journal of Catalysis*, 7(4), 342 – 351, 1967.

- [80] A. Badri, C. Binet, and J.-C. Lavalley. An FTIR study of surface ceria hydroxy groups during a redox process with H<sub>2</sub>. Journal of the Chemical Society, Faraday Transactions, 92, 4669 – 4673, 1996.
- [81] J. Andersson, M. Antonsson, L. Eurenius, E. Olsson, and M. Skoglundh. Deactivation of diesel oxidation catalysts: Vehicle- and synthetic aging correlations. *Applied Catalysis B: Environmental*, 72(1-2), 71 – 81, 2007.
- [82] J. Goldstein, D. E. Newbury, D. C. Joy, C. E. Lyman, P. Echlin, E. Lifshin, L. Sawyer, and J. R. Michael. *Scanning Electron Microscopy and X-ray Microanalysis.* Springer, 2003.
- [83] D. B. Williams and C. B. Carter. Transmission Electron Microscopy. Springer, 2009.
- [84] S. J. Pennycook and P. D. Nellist. Scanning Transmission Electron Microscopy
  Imaging and Analysis. Springer, 2011.
- [85] P. Hartel, H. Rose, and C. Dinges. Conditions and reasons for incoherent imaging in STEM. Ultramicroscopy, 63(2), 93 – 114, 1996.
- [86] H. Rose. Correction of aperture aberrations in magnetic systems with threefold symmetry. Nuclear Instruments and Methods in Physics Research, 187(1), 187 – 199, 1981.
- [87] M. Haider, S. Uhlemann, E. Schwan, H. Rose, B. Kabius, and K. Urban. Electron microscopy image enhanced. *Nature*, 392(6678), 768 – 769, 1998.
- [88] FEI Application Note. https://www.researchgate.net/file. PostFileLoader.html?id=52fe2144d039b184208b45ba&assetKey=AS% 3A272431824998400%401441964216234. Accessed: 2017-07-31.
- [89] W. S Rasband. Imagej, http://imagej.nih.gov/ij/, 1997-2017.
- [90] K. Kimoto, T. Asaka, X. Yu, T. Nagai, Y. Matsui, and K. Ishizuka. Local crystal structure analysis with several picometer precision using scanning transmission electron microscopy. *Ultramicroscopy*, 110(7), 778 – 782, 2010.
- [91] B. Berkels, P. Binev, D. A. Blom, W. Dahmen, R. C. Sharpley, and T. Vogt. Optimized imaging using non-rigid registration. *Ultramicroscopy*, 138, 46 – 56, 2014.
- [92] A. B. Yankovich, B. Berkels, W. Dahmen, P. Binev, S. I. Sanchez, S. A. Bradley, A. Li, I. Szlufarska, and P. M. Voyles. Picometre-precision analysis of scanning transmission electron microscopy images of platinum nanocatalysts. *Nature Communications*, 5, 4155, 2014.

- [93] M. H. F. Overwijk, F. C. van den Heuvel, and C. W. T. Bulle-Lieuwma. Novel scheme for the preparation of transmission electron microscopy specimens with a focused ion beam. *Journal of Vacuum Science & Technology B*, 11(6), 2021 – 2024, 1993.
- [94] R. M. Langford and C. Clinton. In situ lift-out using a FIB-SEM system. Micron, 35(7), 607 – 611, 2004.
- [95] D. T. Gillespie. A general method for numerically simulating the stochastic time evolution of coupled chemical reactions. *Journal of Computational Physics*, 22(4), 403 – 434, 1976.
- [96] M. Jørgensen and H. Grönbeck. Scaling Relations and Kinetic Monte Carlo Simulations To Bridge the Materials Gap in Heterogeneous Catalysis. ACS Catalysis, 7(8), 5054 – 5061, 2017.
- [97] P. Hohenberg and W. Kohn. Inhomogeneous Electron Gas. *Physical Review*, 136, B864 – B871, Nov 1964.
- [98] W. Kohn and L. J. Sham. Self-Consistent Equations Including Exchange and Correlation Effects. *Physical Review*, 140, A1133 – A1138, Nov 1965.
- [99] T. Pingel, M. Skoglundh, H. Grönbeck, and E. Olsson. Revealing local variations in nanoparticle size distributions in supported catalysts: a generic TEM specimen preparation method. *Journal of Microscopy*, 260(2), 125 – 132, 2015.
- [100] E. Xue, K. Seshan, and J.R.H. Ross. Roles of supports, Pt loading and Pt dispersion in the oxidation of NO to NO<sub>2</sub> and of SO<sub>2</sub> to SO<sub>3</sub>. Applied Catalysis B: Environmental, 11(1), 65 79, 1996.
- [101] S. Benard, L. Retailleau, F. Gaillard, P. Vernoux, and A. Giroir-Fendler. Supported platinum catalysts for nitrogen oxide sensors. *Applied Catalysis B: Environmental*, 55(1), 11 – 21, 2005.
- [102] R.M.J. Fiedorow, B.S. Chahar, and S.E. Wanke. The sintering of supported metal catalysts. *Journal of Catalysis*, 51(2), 193 – 202, 1978.
- [103] X. Auvray, T. Pingel, E. Olsson, and L. Olsson. The effect gas composition during thermal aging on the dispersion and NO oxidation activity over Pt/Al<sub>2</sub>O<sub>3</sub> catalysts. *Applied Catalysis B: Environmental*, 129, 517 – 527, 2013.
- [104] Y. Yazawa, N. Takagi, H. Yoshida, S.-I. Komai, A. Satsuma, T. Tanaka, S. Yoshida, and T. Hattori. The support effect on propane combustion over platinum catalyst: control of the oxidation-resistance of platinum by the acid strength of support materials. *Applied Catalysis A: General*, 233(1), 103 – 112, 2002.

- [105] P. Tabib Zadeh Adibi, T. Pingel, E. Olsson, H. Grönbeck, and C. Langhammer. Pt Nanoparticle Sintering and Redispersion on a Heterogeneous Nanostructured Support. *The Journal of Physical Chemistry C*, 120(27), 14918 – 14925, 2016.
- [106] C. M. Yim, C. L. Pang, D. R. Hermoso, C. M. Dover, C. A. Muryn, F. Maccherozzi, S. S. Dhesi, R. Pérez, and G. Thornton. Influence of support morphology on the bonding of molecules to nanoparticles. *Proceedings of the National Academy of Sciences*, 112(26), 7903 – 7908, 2015.
- [107] S. Van Aert, A. De Backer, G. T. Martinez, B. Goris, S. Bals, G. Van Tendeloo, and A. Rosenauer. Procedure to count atoms with trustworthy single-atom sensitivity. *Physical Review B*, 87, 064107, Feb 2013.
- [108] A. De Backer, L. Jones, I. Lobato, T. Altantzis, B. Goris, P. D. Nellist, S. Bals, and S. Van Aert. Three-dimensional atomic models from a single projection using Z-contrast imaging: verification by electron tomography and opportunities. *Nanoscale*, 9(25), 8791 – 8798, 2017.
- [109] Y. Yang, C.-C. Chen, M. C. Scott, C. Ophus, R. Xu, A. Pryor, L. Wu, F. Sun, W. Theis, J. Zhou, M. Eisenbach, P. R. C. Kent, R. F. Sabirianov, H. Zeng, P. Ercius, and J. Miao. Deciphering chemical order/disorder and material properties at the single-atom level. *Nature*, 542(7639), 75 – 79, 2017.
- [110] P. A. Midgley and R. E. Dunin-Borkowski. Electron tomography and holography in materials science. *Nature Materials*, 8(4), 271 – 280, 2009.
- [111] J. C Gonzalez, J. C Hernandez, M. Lopez-Haro, E. del Rio, J. J Delgado, A. B Hungria, S. Trasobares, S. Bernal, P. A Midgley, and J. J. Calvino. 3D Characterization of Gold Nanoparticles Supported on Heavy Metal Oxide Catalysts by HAADF-STEM Electron Tomography. *Angewandte Chemie International Edition*, 48(29), 5313 – 5315, 2009.
- [112] S. Bals, B. Goris, L. M. Liz-Marzan, and G. Van Tendeloo. Three-Dimensional Characterization of Noble-Metal Nanoparticles and their Assemblies by Electron Tomography. Angewandte Chemie International Edition, 53(40), 10600 – 10610, 2014.
- [113] B. Goris, J. De Beenhouwer, A. De Backer, D. Zanaga, K. J. Batenburg, A. Sanchez-Iglesias, L. M. Liz-Marzan, S. Van Aert, S. Bals, J. Sijbers, and G. Van Tendeloo. Measuring Lattice Strain in Three Dimensions through Electron Microscopy. *Nano Letters*, 15(10), 6996 – 7001, 2015.
- [114] M. Alania, A. De Backer, I. Lobato, F. F. Krause, D. Van Dyck, A. Rosenauer, and S. Van Aert. How precise can atoms of a nanocluster be located in

3D using a tilt series of scanning transmission electron microscopy images? Ultramicroscopy, 181, 134 – 143, 2017.

- [115] A. Genc, L. Kovarik, M. Gu, H. Cheng, P. Plachinda, L. Pullan, B. Freitag, and C. Wang. XEDS STEM tomography for 3D chemical characterization of nanoscale particles. *Ultramicroscopy*, 131, 24 – 32, 2013.
- [116] T. J. A. Slater, A. Janssen, P. H. C. Camargo, M. G. Burke, N. J. Zaluzec, and S. J. Haigh. STEM-EDX tomography of bimetallic nanoparticles: A methodological investigation. *Ultramicroscopy*, 162, 61 – 73, 2016.