A Surface science Model for the Phillips Ethylene Polymerization Catalyst

Proefschrift

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Contents

1 Introduction .................................................................................................................. 1
  1.1. Catalysis .................................................................................................................. 1
  1.2. The heterogeneous model catalyst approach ......................................................... 2
  1.3. The Phillips Catalyst ............................................................................................... 5
  1.4. The CrO$_x$/SiO$_2$/Si(100) model for the Phillips ethylene polymerization catalyst – Scope of this thesis .......................................................... 8

2 Experimental ............................................................................................................. 13
  2.1. Preparation of the CrO$_x$/SiO$_2$/Si(100) model catalyst ....................................... 13
  2.2. Spincoating impregnation ....................................................................................... 15
  2.3. Reactors .................................................................................................................. 16
  2.4 Characterization Techniques ................................................................................. 19

3 Thermal activation (calcination) of the CrO$_x$/SiO$_2$/Si(100) model-catalyst .......... 29
  3.1. Introduction ............................................................................................................. 29
  3.2. Experimental .......................................................................................................... 31
  3.3. Results and Interpretation ...................................................................................... 32
  3.4 Discussion .............................................................................................................. 40
  3.5 Conclusions ........................................................................................................... 42

4 Ethylene polymerization with the flat CrO$_x$/SiO$_2$/Si(100) model catalyst ........... 45
  4.1. Introduction ............................................................................................................. 45
  4.2. Experimental .......................................................................................................... 46
  4.3. Activity and Stability ............................................................................................ 49
  4.4. Morphology of polyethylene crystallized from the melt ......................................... 55
  4.5 Ethylene polymerization at low Cr-loading – isolated active sites ......................... 66
  4.6 Conclusions ........................................................................................................... 69
5 Concluding remarks and Outlook ............................................................... 71

5.1. The flat model catalyst approach and the Phillips catalyst ......................... 71

5.2. Ethylene polymerization and the flat CrOₓ / SiO₂ / Si(100) model catalyst ................................................................. 79

5.3. Nascent morphology of polyolefins and the flat CrOₓ / SiO₂ / Si(100)
model catalyst ...................................................................................... 80

5.4. Broadening the scope – catalysis meets polymer physics ......................... 86

Summary .................................................................................................. 92

Samenvatting ............................................................................................ 96

Publications ............................................................................................. 100

Acknowledgement ................................................................................... 101

Curriculum vitae ....................................................................................... 102
Introduction

1.1. Catalysis

A catalyst is probably the closest approximation to the old alchemist dream of the “Stone of Wisdom” capable to turn worthless material into gold. While atomic theory strongly discourages any attempts to directly synthesize gold from anything else but gold ore, catalysis -the active surface- at least can rearrange some chemical bonds in a cheap substrate to produce a higher value product. Intriguingly the catalyst itself comes out of the reaction unchanged so it can rearrange another set of chemical bonds essentially ad infinitum. While a catalyst cannot alter the chemical equilibrium of a given reaction (educt→product) it is a kinetic phenomenon\(^1\) that creates a favorable reaction passway (a transition state of low energy), decreasing the activation barrier and thus increasing the reaction rate. Consequently the reaction can take place at lower temperatures and pressures (if thermodynamic allows it), which decreases investment cost for the chemical plant and required energy. In addition if more than one reaction passway leading to different products (educt→product\(_1\), educt→product\(_2\), …) are possible the catalyst will selectively decrease the activation energy of one of the possible reactions, which alters the selectivity of reaction. In other words a successful catalyst increases the yield of the desired product while diminishing waste. A good example of such catalytic reactions are selective oxidations\(^2\), for example, of ethylene using air and a Ag/α-Al\(_2\)O\(_3\) based catalyst, yielding ethylene oxide (\(\Delta H^{\circ}_{298} = -105\) kJ/mol) instead of the thermodynamically favored full oxidation to CO\(_2\) and water (\(\Delta H^{\circ}_{298} = -1321\) kJ/mol).

Not surprisingly large industries have developed around many catalytic reactions and nowadays products with a total worth of \$3,900,000,000,000\ are produced via catalytic processes\(^3\). Modern industrial catalytic systems are usually the result of extensive yet mainly empirical research and development: industrial research is focussed on exploiting a
catalytic system, not necessarily understanding it. The original catalyst, frequently found by accident, has been optimized for the desired reaction using additives called promotors and is usually supported on a porous high surface area material like active coal, amorphous silica or alumina or crystalline zeolites.

Thus these catalysts tend to be highly complex multiple phase systems that may expose a wide variety of surface species hidden inside the pore structure of the support. Our knowledge about the nature of the reacting surface or the active site and the mechanism of the catalytic reaction is often vague and based on indirect evidence. To gain a deeper understanding we need molecular level information about the catalytic surface but unfortunately only few spectroscopic techniques are available that can operate under reaction conditions and using the industrial catalyst. Furthermore the industrial catalyst is so complex, meaning less defined, that it involves too many interrelated parameters to draw hard conclusion from the limited available database.

1.2. The heterogeneous model catalyst approach

Generally speaking a model catalyst is an idealized version of a real (heterogeneous) catalytic system that has been prepared to gain information, which cannot be obtained using the real system. A model is much simpler than the industrial catalyst: the industrial support is removed or altered, promoting agents and structural aids are missing. This is done to meet the demands of spectroscopic or microscopic techniques and to limit the amount of unknown parameters in the system. Model catalysts are prepared as a compromise between

![Image of catalysts](image)

Figure 1.1
Schematic drawings of (left) a conventional, porous catalyst; (middle) a model supported catalyst with catalytically active phase on a thin layer of support-like material an a flat conducting substrate; (right) a well defined single crystal model of the supported phase, redrawn from ref [14].
two contradictory demands: The desire to achieve atomic definition and control of the surface and the demand to resemble the industrial original to maintain relevance. Model catalysts can be homogeneous, based on well defined organometallic compounds or only exist as a computer algorithm, but for this introduction we will restrict ourself to heterogeneous model catalysts\cite{4,5} that are optimized for the application of surface science and microscopic probes\cite{6,7}.

Ultimate definition models for the active phase are single crystals, with a known geometry of surface atoms depending on direction of the cleavage and the crystal structure e.g. a hexagonal Pt(111), at square Rh(100) surface orientation. A whole battery of powerful surface analysis techniques has developed in the past decades, most of them demand ultra high vacuum (UHV) but a few are also applicable at higher pressures and in some cases under reaction conditions\cite{8}. In UHV, single crystals have been extensively used to study the fundamental adsorption behavior of metal surface and their dependence on surface geometry and composition as well as adsorbate coverage. Lateral interaction of (co-)adsorbates and even elementary surface reactions are investigated on single crystal surfaces\cite{9}.

However, more often than not, single crystals offer only little resemblance with a true catalyst, they are sometimes not even active. This is because the active phase on a “real” catalyst is finely dispersed on the support. Metallic (or non-metallic) clusters of a few nanometers are common and sometimes we find even isolated molecules as active sites, for example, on the Phillips catalyst (CrOₓ / SiO₂). An attempt to incorporate more real world catalysis is made using “model supports” like alumina or silica usually applied as thin films on conducting structural supports. Again two approaches exist emphasizing control or similarity to the industrial catalyst. If hardcore surface science background dictates definition, typical surface science preparation techniques are employed like (reactive) evaporation\cite{10} or electron beam lithography\cite{11-13}. If more emphasis is laid on resemblance with “real life” heterogeneous catalysts, one strives to imitate the industrial catalyst preparation as close as possible in order to maintain the same surface chemistry as on the industrial complement. The model support, often a flat silicon wafer (a Si(100) single crystal covered with a flat, thin film SiO₂), is loaded with the active phase with a wet impregnation technique called spincoating\cite{14,15,17}(section 2) that imitates the widely applied pore volume impregnation used on porous supports like silica gel.
The model catalyst is further activated e.g. by thermal treatment in air (calcination) in much the same way as the industrial counterpart. Replacing the high surface area, non-conducting materials such as silica, alumina and titania by their thin film analogues offers several advantages:

**Figure 1.2**
Analogy between spincoating impregnation of a flat model support and porevolume impregnation of an industrial support.

**Figure 1.3**
Model catalysts based on flat conducting supports are optimized for surface science probes like XPS as the expose all active phase is exposed to the spectroscopy and sample charging is minimized.
• With respect to XPS and other surface spectroscopies the most obvious advantage is that the surface probed in the spectrometer is identical to the catalytic active surface in the reactor. This makes correlation between the catalytic activity and surface characterization straightforward.

• The thin oxide support has sufficient conductivity to minimize the deleterious effects of sample charging on XPS, AES and SIMS measurements.

• The extremely flat surface of the support facilitates the use of scanning probe microscopies to visualize at nanometer detail the supported active phase e.g. the ordaining and size distribution of supported nanoparticles before and after the reaction.

The ultimate goal of this surface science characterization is to create a molecular level picture of the active surface. However, whereas surface spectroscopy and microscopy benefit from the flat, conducting model support, the small catalytically active surface makes it extremely vulnerable for impurities when running catalytic reaction under atmospheric pressure, making the measurement of reproducible catalytic activities the greatest challenge for investigating model catalysts. Only if the model catalyst displays a catalytic activity that resembles that of the industrial counterpart it may claim relevance for the industrial system.

1.3. **The Phillips Catalyst**

The Phillips catalyst has been discovered by Hogan and Banks \[18\] at the Phillips Petroleum Company in the early ‘50s. Today about one third of all high density polyethylene (HDPE) and Linear Low Density polyethylene (LLDPE) is made using Phillips catalysts. The original recipe involved aqueous impregnation of chromic acid on silica, nowadays less poisonous chromium(III) salts are used. Over the years a family of Phillips type catalysts have emerged producing no less than 50 different polyethylenes. This versatility is the reason for the commercial success of the Phillips ethylene polymerization process. The properties of the desired product can be tailored varying parameters like calcination temperature, polymerization temperature and pressure or by variation in the oxidic support e.g. adding titania or simply varying the pore size. However, the sensitivity of the catalysts performance to details in the catalyst preparation has also contributed a great deal to the uncertainty surrounding the molecular level characterization of the supported chromium, the structure of the active site and the mechanism of ethylene polymerization.
1.3.1 Preparation

While chromium can be deposited on the silica support in almost every fashion, including gas phase deposition, the industrial procedure involves pore volume impregnation of high surface area silicas featuring large pore-sizes (Crossfield, Davidson 952) using aqueous chromic acid or nowadays, for safety reasons, basic chromium acetate. The catalyst loading is usually between 0.2 and 1.0 wt% Cr depending on the polymerization process used. If the hydrosopic chromic acid is used, it forms a two dimensional solution on the silica surface featuring equilibrium of chromate, dichromate or even polychromate ions, depending on the chromate loading and the acidity of the support.

The thermal activation of the catalyst, calcination in dry air or oxygen is done in a fluidized bed at temperatures between 500° and 900°C. This treatment will cause the hydrated chromates to anchor to the silica support in an esterfication reaction with the surface hydroxyl groups of the support. If lower valent chromium salts have been used for impregnation they are oxidized during the calcination. The esterfication reaction is already complete at about 200°C, however, at least 500°C is needed to produce significant activity (which further increases until sintering starts at about 950°C). This observation is usually correlated to the decreasing population surface hydroxyls, which are believed to interfere with ethylene polymerization somehow.

Despite continuous and extensive research for more than 40 years now, there is little understanding of the Phillips Catalyst on a molecular level. The reason for this lies probably in the complex redox and coordination chemistry of chromium in combination with the heterogeneous silica surfaces. As a result the supported chromium may be present on the support in a mixture of different valences and coordination environments, depending on the exact preparation. This makes comparison between different groups very difficult and has prevented the development of a unifying picture of the Phillips Catalyst.

The molecular structure of the anchored chromium is still controversial: monochromates, dichromates and even polychromates have been proposed. Scheme 1.4 briefly summarizes the surface chemistry of the Phillips Catalyst, we will take a more detailed look on the relevant literature in section 3.1.
Scheme 1.4
After impregnation with aqueous chromic acid (top) an equilibrium mixture of mono-, di-, and polychromates lay on the fully hydroxylized silica support embedded in a water matrix. Upon calcination water desorbs and the chromium forms surface chromates in an esterification reaction with the surface silanol groups (middle). Whether these surface chromates also form dimers, etc. is not yet clear. Calcination above 500°C yields an active ethylene polymerization catalyst. Upon contact with ethylene at temperatures above 60°C the anchored chromate is reduced, probably to a Cr(II) species. For details see section 3.1 and 5.1.1.
1.3.2 Ethylene Polymerization

There are three different modes of ethylene polymerization using the Phillips catalyst:

The solution process using inert hydrocarbon solvents for the monomer and the polymer (e.g. cyclohexane). This process runs at about 125° - 175°C at a total pressure of 20 – 30 bar. The catalyst is removed from the reactor product by filtration and subsequently the solvent is evaporated from the filtrate. The slurry process uses short paraffins (e.g. butane) to suspend both catalyst and polymer during polymerization at about 15-20 bar ethylene pressure. Temperature is kept below 110°C to prevent swelling of the polymer. Because of the high activity of the catalyst its residue in the polymer is insignificant and is left in the end product. In the gas phase process the catalyst reacts with ethylene in a fluidized bed reactor at about 100°C and 20 bar pressure. While in this process solvent supply and recycling is avoided it is less efficient per unit volume of reactor.

Polymerization of ethylene alone give gives a linear polymer without long chain branching (HDPE) while copolymerization of C₄-C₈ olefins gives a branched polymer (LLDPE). The polymer product usually features a broad molecular weight distribution (Mₘ/Mₚ). The physical properties of the polymer are determined by its average molecular weight, the width of the molecular weight distribution and the amount, type and distribution of side branches. Industrial companies are able to tailor their Phillips process to produce polymer properties according to their customers specifications, based on a wealth of empirical knowledge gathered over the decenia.

1.4. The \( \text{CrO}_x/\text{SiO}_2/\text{Si(100)} \) model for the Phillips ethylene polymerization catalyst – Scope of this thesis

Over the last few years our group has build up experience with what we call realistic model supports. The aim of this version of the model catalyst approach is to mimic the industrial preparation of a catalytic system. This approach involves a wet impregnation technique called spincoating impregnation on flat thin film oxide model support. The further pretreatment follows the industrial recipe as close possible and finally the catalyst is tested for catalytic activity in much the same way as the industrial counterpart. The molecular state of the active surface is monitored at molecular level detail using surface science techniques such as X-ray Photoelectron Spectroscopy (XPS), Secondary Ion Mass Spectroscopy (SIMS) and Atomic Force Microscopy (AFM). The ultimate goal of this approach is to link the preparation parameters to a molecular structure of the catalyst and to
the catalytic performance\textsuperscript{(16)}. This approach has already successfully been applied to model hydrodesulfuridization catalysts of the CoMoS type\textsuperscript{(19,20)}.

The CrO\textsubscript{x} / SiO\textsubscript{2} system presented an ideal challenge to further explore the possibilities of flat model catalyst approach:

- It is an oxidic active phase, which sets this model system apart from the main body of surface science model catalysts, which deals with supported metal particles.
- As the Phillips catalyst is an ethylene polymerization catalyst, the model system is to produce thin films of polymer. Characterizing these polymers could become a topic in its own right.
- The performance of the Phillips catalyst is extremely sensitive towards the exact preparation, however, the molecular level picture of the catalyst and its precursors is still rather vague (see section 3.1 and 5.1.3.).

Not only the amount of polymer produced (activity of the catalyst) but also the properties of the polymer, its molecular weight (M\textsubscript{w}), the molecular weight distribution (M\textsubscript{w}/M\textsubscript{n}) and the amount of side branching (selectivity) depend on the exact mode of polymerization and on the catalyst preparation. The Phillips catalyst features as little as 1 wt\% of chromium on a large pore silica gel, which corresponds to an average coverage of less than 1 Cr/nm\textsuperscript{2}. To visualize such a small amount of chromium presents somewhat of a challenge to the surface spectroscopist, a flat catalyst with all active phase accessible to surface characterization represents a significant advantage.

The scope of this project was twofold:

- Explore the CrO\textsubscript{x} / SiO\textsubscript{2} system using the surface science model catalyst approach.
- Doing so test the feasibility of this concept by applying it to an industrial important catalyst that has remained somewhat of black box despite continual academic and industrial research over almost half a century.

Hence this thesis covers the preparation, UHV characterization, catalytic testing of the CrO\textsubscript{x} / SiO\textsubscript{2} / Si(100) model of the Phillips ethylene polymerization catalyst. Chapter 2 covers the experimental details of the employed surface probes as well as the experimental tools that we developed to handle this somewhat delicate catalytic system. In section 3 we describe the thermal activation of the model catalyst. This study reveals the structure of the silica bound chromium species being monochromate exclusively, with desorption of
chromium acting as a mechanism to isolate the active species. In section 4 we address ethylene polymerization over the CrO$_x$/SiO$_2$/Si(100) catalyst. The model system features a reasonable catalytic activity at 160°C, comparable to the industrial catalyst. The polymer films that evolve during polymerization are well suited for atomic force microscopy. They develop the expected morphology for melt crystallized polyethylene, however at nanometer resolution we observe, for the first time for polyethylene, a substructure in the lamellar crystal architecture. Finally in section 5 we try to point out some possible future developments of the flat model catalyst approach that either directly concern the CrO$_x$/SiO$_2$/Si(100) system or at least have been inspired by it.

Reference List

2

Experimental

2.1. Preparation of the CrOₓ / SiO₂ / Si(100) model catalyst

The preparation of the CrOₓ / SiO₂ / Si(100) model catalyst (scheme 2.1) starts from a silicon single disk of 10 cm diameter with (100) surface orientation. This disk is first calcined in air at 750°C for 24 hours to produce a thin film (up to 90 nm) of amorphous oxide. The calcined SiO₂ / Si(100) wafers expose a hydrophobic surface that consists of siloxane groups (Si-O-Si). In order to make the surface hydrophilic (necessary to apply spincoating impregnation from aqueous solution) the wafers are treated with a mixture 1/1 (vol/vol, ± 250 ml) of H₂O₂ (25%, p.a., Across) and concentrated ammonia (NH₄OH, 33%, p.a., Merck), that is heated to up to 65°C. During this procedure the peroxide rapidly (!!!) decomposes and oxidizes the organic layer of the ubiquitous carbon on the silica surface, while a few nanometer of silica dissolve in the strongly basic solution. The reaction is quenched with ± 250 ml water (millipore) and the wafers are subsequently transferred into boiling water (keeping the surface under a water or impregnating solution at all times) and subsequently to the impregnation solution, 0 – 10 mmol CrO₃ in water. The wafers can be kept in the spincoating solution for up to 1 day. For spincoating the wafer (covered with the spincoating solution) is mounted onto an electric motor under dry nitrogen atmosphere and spun at 2800 r.p.m. Most of the solution is ejected from the wafer leaving behind a thin film that evaporates within about 7.5 seconds leaving behind the solute: 1 Cr/nm² for every mmol (CrO₃)/l (spincoating impregnation, → 2.2.). The catalyst is activated for ethylene polymerization though calcination in dry Ar/O₂. This is done either in a quartz reactor for subsequent polymerization in one bar of ethylene, or in a reactor built in the transfer chamber of a VG Escalab 200 spectrometer to allow surface analysis of the activated catalyst without transport through the air or a glovebox. Both reactors are described in the detail in the following sections.
Scheme 2.1
Preparation, activation and testing of the CrO$_x$/SiO$_2$/Si(100) model catalyst. Details are described in the text.
2.2. Spincoating impregnation

Spincoating is a well-known technique for preparation of uniform films and is applied in industry to deposit layers of polymeric photo-resist on silicon wafers. It has been developed as an impregnation technique to deposit active phase from dilute solution on a flat model catalyst by Kuipers et al. \cite{1,2} and van Hardeveld et al. \cite{3}. It turns out that it can be modeled, allowing accurate predictions (± 10%) of the amount of the material eventually deposited\cite{3} (verified by Rutherford backscattering). As the solution is ejected from the spinning disk (radial flow, scheme 2.2) the balance between centrifugal and shear forces in the steady state of spincoating leads to a decrease in film height $h$ proportional to $h^3$.

Simultaneously, there is a constant loss of solvent due to evaporation. There is a point in time $t_e$, at which these contributions are equal, and in first approximation, one can assume that before $t_e$ evaporation is negligible, while after $t_e$ evaporation is the only source of decrease in film height. Solving the resulting differential equation shows that the amount of deposited material is proportional to the concentration of the spincoating solution and inversely proportional to the square-root of the evaporation time. For spincoating from aqueous CrO$_3$ solution at room temperature using a spinning speed of 2800 r.p.m. we arrive at:

$$ L_{Cr} = 2.76 \times \left( t_{\text{evap}} \right)^{-0.5} \times C_0 $$

\textit{Equation 2-1}

\textbf{Scheme 2.2}

Evaporation of the solvent and radial liquid flow (due to centrifugal forces) of the solution determine the amount of solute, which precipitates on the wafer. Redrawn from\cite{3}.

![Scheme 2.2](image)
where $L_{Cr}$ is the loading of the wafer in Cr-atoms/nm$^2$, $t_{evap}$ is the evaporation time in seconds, and $C_0$ is the concentration of the spincoating solution in mmol/l. The evaporation time ($\pm$ 7.5s) can be measured monitoring the disappearance of the Newton rings, which become visible, when the liquid layer is sufficiently thin. All catalyst loadings of the CrO$_x$/SiO$_2$/Si(100) catalyst have been determined from equation 2.1.

### 2.3. Reactors

The impregnated catalyst must be calcined in dry air or oxygen at temperatures above 450°C to become an active ethylene polymerization catalyst. According to general consensus surface chromates are formed during this thermal activation in an esterification reaction with the surface silanol groups of the silica support. The calcined catalyst is very sensitive against trace amounts of water that can easily rehydroxylate the surface chromate rendering an inactive catalyst. CrO$_3$ is also easily reduced by organic matter that is present in almost every environment (“ubiquitous carbon” is a common internal reference in X-ray photoelectron spectroscopy). During olefin polymerization the active catalyst becomes even more delicate as the coordinatively unsaturated chromium easily reacts with impurities in the gas feed (e.g. H$_2$O, O$_2$, C$_2$H$_2$, CO) that act as catalyst poisons. On laboratory scale, high surface area catalysts are used in amounts of a few hundred mg representing a few ten up to a few hundred µmol of active phase. These catalysts tolerate impurities in the ppm range and can be routinely handled in e.g. a glove box.

The CrO$_x$/SiO$_2$/Si(100) model catalyst however features only a very small active surface in the order of 1 cm$^2$. This corresponds to no more than 1 nanomole of supported chromium. At 1 bar, 1 cm$^3$ of gas feed containing 1 ppm of a given poison is enough to deactivate 5% of the active chromium. Acknowledging this delicacy of our model system we designed 2 dedicated reactors. One reactor was built into the transfer chamber of the VG Escalab 200 spectrometer (section 2.2.1) to facilitate transfer of the activated catalyst to UHV environment without exposure to air or glove-box ambient. The second reactor was made to facilitate catalyst activation and olefin polymerization in one reactor. Both reactors had to meet quite stringent specifications to meet the specific demands of the CrO$_x$/SiO$_2$/Si(100) model catalyst. Reactor design - the preparation side of model catalysis - is usually less prominent than the expensive surface spectroscopies. However it is the pre requisite to ensure relevance of the ex-situ (?) surface science characterization of the model catalyst and thus determines the future potential of the realistic model catalyst approach.
2.3.1 High temperature reactor built in the transfer chamber of the VG Escalab 200 spectrometer

Figure 2.3 shows a schematic view of the reactor that was fitted into the transfer chamber of the VGX 200 spectrometer. From here the activated catalyst can be directly transferred to the XPS analysis chamber or it can be moved to the VG-SIMS spectrometer using a sealed transfer vessel.

A heating rod is fitted into a cylinder made of super alloy 2000. This alloy consisting of iron, chromium, aluminium and yttrium oxide forms an inert alumina passivation layer when heated in air to temperatures above 800°C. Two thin bores (along the axis of the cylinder) serve as gas inlet and outlet, respectively. A small hole on the top face of the cylinder can hold one VG-type sample holder (made of titanium) supporting one piece of CrO$_x$/SiO$_2$/Si(100) model catalyst ($\pm 1$ cm$^2$, held in place by a screw). A thermocouple placed near the top surface of the metal cylinder controls the temperature, a second one

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**Figure 2.3**
Schematic view of the calcination reactor that is built in the preparation chamber of the VG escalab 200 spectrometer. A heating rod heats a metal cylinder, covered by a thin passivation layer of alumina (super alloy 2000). Two small drillings on the sides of the cylinder serve as gas-in and -outlet, respectively. The cylinder can hold one sample, mounted on a titanium sample holder. The reactor is closed by a movable hood (superalloy 2000) that is attached to a liner drive. It can operate at up to 1 bar O$_2$/Ar or CO and 730°C.
placed near the heating zone prevents overheating of the heating rod. The reactor can be sealed with a movable hood (superalloy 2000) mounted on a linear drive. It can be heated to 730°C at atmospheric pressure of artificial air (O₂/Ar, 80/20, 5.0, Hoekloos, dried over molecular sieves 4A) or carbon monoxide (CO, 5.0, Hoekloos, purified over BASF Catalyst R 3-11, Chrompack and molecular sieve 4A). The bottom (heating) and the top (hood) part of the reactor are firmly stuck together when working at high temperatures and therefore can only be opened after cool-down to 100°C.

2.3.2 Quartz reactor for ethylene polymerization

Figure 2.4 shows the reactor used for the activation of the catalyst and the actual polymerization. It consists of two quartz tubes of 4 and 1 cm in diameter, respectively. The larger tube is surrounded by resistive heating cable and is closed on one side. The other side allows access to the thin tube and two gas valves, one connecting the reactor to a turbo-molecular pump, the other serving as gas exhaust during flow operation. The thin tube extends into the heated zone. Behind a quartz filter, the tube broadens to support up to 6 model catalysts. A chromel/alumel thermocouple, protected by a thin quartz tube, measures the temperature at this point. Before the quartz filter, upstream as seen from the model catalysts and within the heating zone, the thin tube is filled with γ-alumina extrudates.

Figure 2.4
Ethylene polymerization reactor made of quartz. Key feature is the column of chromium loaded γ-alumina-extrudates, which serves as catalytic filter to remove poisons from the gas feed. Activation of the catalyst by calcination at 450°-650°C is also done in this reactor.
impregnated with 0.17 wt% chromium (by incipient wetness impregnation from basic chromium(III) acetate solution). The chromium-loaded γ-alumina serves as a filter for the impurities in the ethylene feed stream. The reactor is sealed against atmosphere using viton O-rings.

Before the reactor is loaded with the model catalyst, it is dried in vacuum to 200°C and subsequently baked out at 750°C in flowing O$_2$/Ar (20% O$_2$, dried with molsieves 4A), to remove water and sodium from the reactor walls. Next the model catalyst is inserted. After drying at 200°C in vacuum, the catalyst is calcined in flowing O$_2$/Ar at 550°C for 30 min (heating rate 20K/min, plateau at 450°C for 15 min). After cooling to 160°C the gas flow is stopped and the O$_2$/Ar is exchanged to argon (purified over a copper catalyst and a molecular sieve of 4A) and subsequently to ethylene. The gas exchange takes about 2 minutes, making the start time for the polymerization reaction uncertain to within at least one minute. Polymerization takes place in flowing ethylene at 160°C and at atmospheric pressure. Pumping away the ethylene and changing to argon atmosphere stops the reaction. The polyethylene formed on the catalyst surface is initially present as a molten film and is allowed to crystallize at 100°C for 2h before the reactor is cooled to room temperature.

### 2.4 Characterization Techniques

In this thesis the catalyst and the produced polymer have been characterized with a combination of X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), secondary ion mass spectrometry (SIMS), Rutherford backscattering spectrometry (RBS) and infra red spectrometry (FT-IR). The experimental details of these techniques are given in chapters 3 and 4. The principle of all employed techniques is nicely explained in [4], however we want to briefly discuss the two main techniques used in this thesis, XPS and AFM to give some details of our data handling.

#### 2.3.1. X-ray photoelectron spectroscopy (XPS)

**General**

X-ray photo electron spectroscopy [4,5] is probably the most widely applied surface science technique as it provides qualitative and semi-quantitative information about the amount and chemical state of the elements present in the surface region of a sample. It is based on the
photoelectric effect, in which an atom absorbs a photon of energy $h\nu$ (e.g. Al Kα = 1486.6 eV) under the emission of a core or valence electron with the kinetic energy:

$$E_k = h\nu - E_b - \phi$$  \hspace{1cm} \text{Equation 2-2}

with:

- $E_k$ = kinetic energy of the photoelectron
- $h\nu$ = energy of exciting radiation
- $E_b$ = binding energy of photoelectron
- $\phi$ = workfunction of the spectrometer

An XPS spectrum is usually a plot of the photoelectron intensity versus the binding energy $E_b$. The binding energy is element specific and in addition shows small changes (up to a few eV), usually referred to as chemical shift, depending on the charge and chemical environment of the atom in question. The interpretation of chemical shifts is most revealing if done comparing to binding energies of well-chosen reference compounds. The intensity of a photoelectron peak can be expressed as:

$$I = F_X S(E_k) \sigma(E_k) \int_0^\infty n(z) e^{-z/\lambda(E_k)\cos\theta} \, dz$$ \hspace{1cm} \text{Equation 2-3}

with:

- $I$ = the intensity of the XPS peak (area)
- $F_X$ = the X-ray flux on the sample
- $S(E_k)$ = transmission function of the spectrometer
- $\sigma(E_k)$ = cross section for photoemission
- $n(z)$ = number of atoms per unit volume
- $z$ = depth below surface
- $\lambda(E_k,z)$ = mean inelastic free path of photoelectron through the material at depth $z$
- $\theta$ = angle between direction of tin which the photoelectron is emitted and the surface normal

Thus the intensity of the XPS peak depends on the spectrometer, the cross section of the element, its concentration and distribution in the surface region, the exponential term in equation 2.3 corresponds to the escape probability of the photoelectron, which decreases
Experimental with increasing depth of the emitting atom below the surface. The mean free path of an electron $\lambda$, corresponds to the average distance an electron can travel through a material without losing energy due to inelastic interactions. Quantification of the XPS spectra is usually based on intensity ratios of relevant XPS peaks ($I_A/I_B$) thereby assuming a certain (simple) distribution of A and B in the surface region of the sample, (e.g. homogeneous distribution of A and B, a homogeneously thick layer of A on substrate B or a fractional monolayer of A on a flat substrate B). In this thesis we will only use the last case, as we could establish that the supported chromium oxide (especially after calcination) is molecularly dispersed on the silica support (section 3).

**XPS of the CrO$_x$ / SiO$_2$ / Si(100) model catalyst**

XPS-spectra were collected in a VG-Escalab 200 Spectrometer using an aluminium anode ($\text{Al K}\alpha = 1486.6$ eV). All XPS spectra shown in this thesis are charge corrected ($< 1.5$ eV) referring to the Si 2p peak of SiO$_2$ at 103.3 eV, and also normalized with respect to intensity (integrated peak area) of the Si 2p emission. Even though the silica layer of the

![Wide scan of the SiO$_2$ / Si(100) model support](image)

*Figure 2.5 Wide scan of a SiO$_2$ / Si(100) model support. The inlets show the Si 2p emission and the electron energy loss tail of the O 1s emission that causes a non-linear background for the Cr 2p emission and has to be subtracted before analysis.*
SiO$_2$ / Si(100) model support is up to 90 nm thick, the Si 2p peak of silica layer remains narrow (FWHM = 1.85 eV at 20 eV pass energy, inset figure 2.5). The Cr 2p window is measured at 50 eV pass energy to obtain an acceptable signal to noise ratio as the measurement time is limited to 10 minutes due to rapid degradation of the supported chromate under the XPS beam. Before quantification of the Cr 2p emission, the underlying O 1s energy-loss structure has been removed using a blank reference (figure 2.6). The thus obtained Cr 2p spectra were analysed using the XPSPEAK95 software developed by R.W.M. Kwok (version 3.1; available on the Internet as freeware) using a Shirley background correction. After subtraction of the blank reference spectrum (SiO$_2$ / Si(100)) the Cr 2p emission showed the expected 2/1 intensity ratio for Cr 2p$_{3/2}$ / Cr2p$_{1/2}$.

![Figure 2.6](image)

*Figure 2.6*

After charge correction (silica, Si 2p = 103.3 eV) and normalization (I (Si 2p) = 1) the O 1s electron loss background is removed from the Cr 2p emission by subtraction of a blank reference. This procedure yields “well behaved” Cr 2p spectra that show the expected 2/1 ratio for the intensity of the 2p$_{3/2}$ and 2p$_{1/2}$ peaks.
2.3.2. AFM

Atomic force microscopy (AFM) images were taken on a Digital Instruments Dimension 3100 scanning microscope under ambient conditions (figure 2.7). Measurements, performed in tapping mode (height images, amplitude or phase contrast as indicated on the images), were recorded by using etched Si$_3$N$_4$ tips (TESP) with a force constant of about 20-100 N/m. Polyethylene layer thickness was determined using the height difference between the Si-substrate and the polyethylene surface after scratching the layer with a scalpel (section 4.3.2).

**Principle and visualization contrasts in tapping mode AFM**

In tapping mode, the cantilever is excited into resonance oscillation with a piezoelectric driver while scanning above the sample surface in a raster-like fashion (figure 2.8). Upon contact with the sample surface the amplitude will decrease as the AFM-tip hits the surface (tapping) as compared to the free amplitude of the unperturbed tip. While scanning above the surface, the oscillation amplitude is used as a feedback signal to measure topographic variations of the sample, the oscillating piezo driver adjusts the height of the cantilever above the surface to restore the preset amplitude of the AFM-tip. Amplitude of the AFM-tip oscillation and height of the cantilever are simultaneously recorded to yield an image of the surface in height and amplitude contrast. Height contrast gives quantitative information about the topography of the surface (e.g. particles size and distribution on a flat surface). Especially the height information is very accurate ($\pm$ 0.01 nm), however, the lateral image of the particles in the AFM image is always a convolution of the true particle shape and the tip shape. Very sharp features on the surface yield images of the AFM-tip rather than the other way around. Conversely, on extremely smooth surface AFM can reach even atomic resolution. Amplitude contrast gives no straight forward physical information of the surface, however, it usually shows a superior contrast to height images, showing small details of the topography even if large height variations are present on the surface. It represents somewhat of a differentiated version of a height image as the amplitude of the AFM-tip responds to height changes on the surface. In phase imaging, the phase lag of the cantilever oscillation, relative to the signal sent to the cantilever’s piezo driver, is simultaneously monitored. The phase lag is very sensitive to variations in material properties such as adhesion and viscoelasticity, consequently the phase imaging can be used to discriminate between component phases of semi-crystalline polymers such as
polyethylene (e.g. soft amorphous part vs. hard crystalline part in lamella crystals (→
section 4.4)).

Figure 2.7

Figure 2.8
Schematic impression of the three visualization contrast modes in tapping-mode AFM.
Upon contact with the sample surface the AFM tip will oscillate at a reduced amplitude
that is used as a feed-back signal to adjust the height of the cantilever above the surface
$(h_0 \pm \Delta h)$ while scanning over the surface. This creates the height-image of the sample.
The variation of the amplitude gives the amplitude image. In phase contrast variations in
the phase lag between piezo driver and AFM tip are mapped.
Size determination of isolated polymer islands on the CrO$_x$ / SiO$_2$ / Si(100) model catalyst

In section 4.5 we use AFM to determine the volume of isolated polymer islands that we consider be the product of individual active sites. These isolated polymer islands appear circular in top view with a height between 2 and 4 nm and a base-diameter between 30 and 60 nm. As these polymer islands are imaged by an AFM tip with a tip radius of 5-10 nm we want to estimate the contribution of the tip-error to the apparent island size.

**Figure 2.9**

An isolated PE-island (left), measured by AFM (tip curvature radius: $p$=5-10 nm) appears as a paraboloid with a height ($h$) of 3.1 nm and a diameter of 52 nm (radius $r_{y=0}$ = 26 nm). To estimate the contribution of the sample tip (tip error: $X$) to the apparent radius, assuming a cylindrical particle shape, we have plotted $p \rightarrow X$ for different heights of the cylinder. We conclude that the observed particle shape cannot be explained in terms of tip/sample deconvolution using a cylindrical peak shape, their height profile would look like the dotted line in the top left panel. The observed peak shape is a much better approximation of the true peak shape due to the very shallow slope of its flanks.
If we assume a cylindrical particle shape the tip error of the island-radius would be between 6 and 10 nanometer (figure 2.9, right panel) resulting in a horizontal plateau in the center of the island. The cross section of the AFM images, however, is a smooth parabola with a very large curvature-radius \( p \approx 100 \text{ nm} \) as compared to the tip (figure 2.9, left panel) indicating that the AFM image is a good representation of the actual particle shape. Still the AFM tip contributes for the observed base-radius of the polymer island as depicted in figure 2.10. AFM microscopy overestimates the base radius if the polymer island by about 1 nm, about the same size as our experimental error. As already mentioned the height of the polymer particle can be measured with higher accuracy (± 0.1 nm). The volume of the polymer particle is \( V = \frac{\pi}{2} h r_{(y=0)}^2 \) and can be determined with this method with an accuracy of ± (10 - 20)%.

*Figure 2.10*

The isolated polymer island depicted in the top-left panel can be approximated by a paraboloid with a height of 3.1 nm and a base radius of 26 nm. The AFM tip still overestimates the base radius of the particle by about 1 nm.
Reference List

Thermal activation (calcination) of the \( \text{CrO}_x/\text{SiO}_2/\text{Si}(100) \) model-catalyst

3.1. Introduction

Highly dispersed chromium oxide supported on silica is an industrially important catalyst for ethylene polymerization. This well-known Phillips Catalyst\(^{[1,2]}\) produces roughly one third of the world supply of linear high density polyethylene. It consists of less than 1 wt\% Cr, impregnated commonly as an aqueous solution of \( \text{CrO}_3 \) or \( \text{Cr(III)} \)-salts on high surface area silica (\( \pm300 \text{ m}^2/\text{g} \)), which corresponds to about 0.4 Cr/nm\(^2\) only. The catalyst is activated through calcination in dry air or oxygen and polymerizes ethylene e.g. in a loop reactor at 35 bar and 110°C in isobutane slurry (Phillips Process).

Despite continuous and extensive research for more than 40 years now, there is little understanding of the Phillips Catalyst on a molecular level. The reason for this lies probably in the complex redox and coordination chemistry of chromium in combination with the heterogeneous silica surfaces. As a result the supported chromium may be present on the support in a mixture of different valences and coordination environments, depending on the exact preparation. The nature of the silica support (e.g. specific surface area, porosity and concentration of surface hydroxyls), the Cr-loading, the activation method (e.g. maximum temperature, heating rate, total calcination time and calcination atmosphere) and further chemical treatments (e.g. reduction with \( \text{C}_2\text{H}_4 \), CO, H\(_2\) or metal alkyls, temperature, etc.) all influence the chemical state of the supported chromium. Consequently, results obtained by different groups, each preparing their own “Phillips catalyst”, are difficult to compare and there is still controversy about the state of the supported chromium species after activation.
There is, however, a general consensus that during calcination the supported chromium can anchor to the silica support in an esterfication reaction with the surface hydroxyl- groups yielding surface chromate(VI) species. The maximum amount of chromate that is anchored to the support is limited by the amount of hydroxyls available and will decrease with increasing temperature (if lower valent chromium precursors have been impregnated the chromium will be oxidized during the calcination). If a fully hydroxylized silica is used the saturation coverage at 425°C is about 1.8 - 2.3 Cr/µm², the excess chrome is converted to chromium(III)-oxide\[1\]. The structure of the surface chromate, in particular the degree of polymerization, remained disputed in the literature over the years. Indirect evidence has been deduced from measuring the change in hydroxyl population upon binding of the chromium or by the reverse reaction, stripping of anchored chromium using hydrogen chloride\[1,3-5\]. The general trend in these experiments is that chromate anchors to the silica surface initially as monochromate while high calcination temperatures and loadings encourage the formation of dichromates.

In the 90’s the molecular structure of anchored chromium on various supports has been intensively studied with spectroscopic techniques such as Raman - or UV-Vis spectroscopy \[6,7\] (and references therein). Again it is difficult to compare to other authors because the surface area of the substrates varies strongly and their hydroxyl population remains unknown. For silica both monochromate (on a precalcined Cab-O-Sil) and dichromate (on a precalcined sol-gel silica) have been found to be the main species after calcination. Again high chromium loading and calcination temperatures are believed to favor the formation of surface dichromates. However, these very conditions also lead to the formation of Cr₂O₃, which can also form surface chromates. This makes the assignment of surface dichromates questionable, since the employed techniques, Raman and diffuse reflectance UV-vis do not discriminate between chromates on a silica or chromia surface.

Ultra high vacuum spectroscopic techniques are potentially very powerful for the desired microscopic characterization of catalysts in general, as they provide direct information originating from the atoms and molecules on the surface. To use these techniques at their full potential we have chosen to prepare a flat model catalyst based on a conducting silicon single crystal covered with a thin film of amorphous silica.

Replacing high surface area, non-conducting materials such as silica, alumina and titania by their thin film analogues offers several advantages: With respect to XPS and other surface
spectroscopies the most obvious advantage is that the surface probed in the spectrometer is identical to the catalytically active surface in the reactor. This makes correlation between the catalytic activity and surface characterization straightforward.

The active phase is deposited onto the model surface from a homogeneously thick evaporation layer resulting in a homogenous catalyst loading in the nanometer-scale. The wide distribution of pore sizes in a silica gel results in equally large variation of catalyst loading and dispersion. The superior definition of the active phase on the model catalyst improves the resolution of e.g. photoelectron peaks. The thin oxide support has sufficient conductivity to minimize the deleterious effects of sample charging on XPS, AES and SIMS measurements.

Our surface science model is impregnated with aqueous CrO$_3$ using the spincoating technique [8-10], which gives control over Cr-loading and mimics the conventional pore-volume impregnation used in industry for high surface-area silica gels. This model catalyst shows a realistic catalytic activity for ethylene polymerization. The scope of this chapter is to look at the calcination (activation) of the Phillips catalyst on a molecular scale, using our flat model-catalyst and surface science techniques.

### 3.2. Experimental

#### 3.2.1. Preparation of the Cr$_{ox}$/SiO$_2$/Si(100)-model

CrO$_2$/SiO$_2$/Si with a Cr-loading between 0.4 and 10 Cr/nm$^2$ are prepared from aqueous CrO$_3$ (0.4 -10 mmol/l) using spincoating impregnation at 2800 r.p.m. in dry nitrogen. The samples were calcined in a homemade preparation chamber that is directly connected to a VG-Escalab 200 spectrometer. Heating occurred stepwise in 100 K steps starting at 150°C upto the desired calcination temperature. Each plateau was held for half an hour to allow equilibration of the reactor. For details see chapter 2.

**XPS**

XPS measurements were done with a background pressure of 5 × 10$^{-10}$ mbar using an aluminum anode (Al K$_\alpha$ = 1486.3 eV) operating at 510 VA. Since Cr[VI]-oxide decomposes rapidly (within 10 minutes) when exposed to X-rays. To minimize the effect of degradation individual scans of the Cr 2p were added until the damage becomes visible. All
binding energies are referred to the Si 2p at 103.3 eV (SiO$_2$) to correct for charging (< 1 eV). Intensities are normalized to the total Si 2p area.

**SIMS.**

Secondary Ion Mass Spectrometry (SIMS) was performed in a VG Ionex system equipped with a VG 12-12S quadrupole mass spectrometer and a VG FAB61 fast atom bombardment source. The base pressure of the analyzing chamber was 1x10$^{-9}$ mbar. Samples were transported to this separate chamber using a sealed transfer vessel. A 5keV Ar$^+$ ion beam was used for all spectra. Charge compensation by a low energy electron flood gun was not necessary. The blank sample was measured using dynamic SIMS with a beam current density of about 3µA/cm$^2$ enhancing secondary ion yield in order to ensure the detection of all Si$_x$O$_y$ fragments. Spectra of the Cr loaded samples were taken under quasi-static conditions applying beam current densities of approximately 50nA/cm$^2$ to avoid rapid surface damaging. The target bias was adjusted for maximum intensity of mass 100 (CrO$_3$) and 136 (Si$_x$O$_y$) signals in negative SIMS. The displayed spectra are normalised to the 136 amu signal.

**RBS**

Samples for Rutherford Backscattering Spectrometry (RBS) were prepared in a quartz tube reactor described in [11]. RBS spectra were measured with an incident beam of 2 MeV He$^+$, produced with the AVF-cyclotron at the Eindhoven University of Technology [12]. Details concerning beam optics and detectors have been published in [13]. The overall energy resolution was measured to be 22 keV. We adopted a scattering geometry with the incoming beam directed 5° from the surface normal and a scattering angle of 150°. We assume that the cross-sections are accurate within 4%.

### 3.3. Results and Interpretation

#### 3.3.1. X-ray Photoelectron Spectroscopy (XPS)

The X-ray photoelectron spectra in figure 3.1 show the Cr 2p emission of Cr$_{ox}$/SiO$_2$/Si(100)- models and of three Cr(VI) references. After spincoat impregnation of 1 CrO$_3$/nm$^2$ the Cr 2p peak appears at 580.0 eV, the same binding energy that we measured for bulk CrO$_3$ or alkali chromates. Upon calcination at 450°C the binding energy increases
to 581.3 eV. This binding energy is in excellent agreement with the 581.6 eV (with Si 2p = 103.5 eV) measured by Merryfield et al.\cite{14} for a 1.1 wt% Cr/SiO$_2$ (0.42 Cr/nm$^2$) catalyst calcined in dry air at 650°C.

![Figure 3.1](image1.png)

**Figure 3.1**
Cr 2p spectra of the CrO$_x$/SiO$_2$/Si(100) model catalyst and of some Chromate(VI) - type reference compounds. Impregnated chromate features the same binding energy as alkali chromates/dicromates or bulk CrO$_3$. Upon calcination this binding energy increases by 1.3 eV. This unusually high binding energy is typical for chromate(VI) forming ester bonds to silica as in [CrO$_4$(OSi(C$_6$H$_5$)$_2$OSi(C$_6$H$_5$)$_2$O)$_2$]$_2$ and has no parallel for chromate on other oxidic supports!

![Figure 3.2](image2.png)

**Figure 3.2**
The normalized Cr 2p intensity exhibits a linear correlation with the catalyst loading below 2 Cr/nm$^2$, implying molecular dispersion of chromate on the silica support in the low coverage regime. This holds for both impregnated and calcined (450°C) catalyst.
Moreover we measured a siloxane-ester of chromic acid ([CrO$_2$(OSi(C$_6$H$_5$)$_2$OSi(C$_6$H$_5$)$_2$O)$_2$])$_2$ as a reference for surface chromium(VI)-esters, which turned out to have the same Cr 2p$^{3/2}$ binding energy as the anchored chromate on silica. Thus we conclude that the shift in Cr 2p$^{3/2}$ binding energy from 580.0 to 581.3 eV proves the anchoring of Cr to our SiO$_2$/Si(100)-model support upon calcination. The high binding energy of surface chromate is a unique feature of the silica support whereas chromate on other oxidic supports like Al$_2$O$_3$ or SnO$_2$ show Cr 2p$^{3/2}$ maxima close to 580 eV.

Figure 3.3
Development of the Cr 2p emission of a model catalyst with 4 Cr/nm$^2$ in time during calcination at 450°C.

The broad peak centered at 580 eV after impregnation splits into two components after calcination at 5 minutes. The shoulder at 577.7 eV assigned to Cr$^{III}$-oxide clusters disappears upon further calcination, while the high binding energy peak shifts from 581.0 to 581.4 eV assigned to silica bound surface chromate. After 30 minutes only 2.4 Cr/nm$^2$ is detected.

Figure 3.4
Increasing the calcination temperature leads to a further decrease (see fig. 3.3) of Cr 2p intensity, while peak maximum and shape remain constant.
The intensity of the Cr 2p emission for given chromium loading is a measure for the dispersion of Cr on the silica surface. Figure 3.2 shows the intensity of the Cr 2p emission as a function of the chromium loading. For low loadings both the hydrated (as spincoated) and the dehydrated (calcined at 450°C) catalyst show the expected linear correlation indicative of molecular dispersion. The extreme solubility of chromium trioxide in water prevents the formation of particles on the hydrated catalyst; after calcination the chromium is expected to anchor to the support, which ensures molecular dispersion. Indeed, the molecular dispersion of the calcined catalyst ends at about 2 Cr/nm$^2$, which is in nice agreement with the 1.8 – 2.3 Cr/nm$^2$ reported by McDaniel for fully hydroxylized silicas\cite{1}.

While on high surface area silicas the superficial chromium is converted to Cr$_2$O$_3$, the XPS shows a different behavior for our flat model catalyst as illustrated in figure 3.3. Model catalysts with 4 Cr/nm$^2$ initial loading are calcined at 450°C. The hydrated catalyst (after spincoat impregnation) shows a broad Cr 2p emission with a Cr$_{2p3/2}$ peak at 580 eV. After 5 minutes at 450°C the Cr$_{2p3/2}$ peak has split into two components with a peak maximum at 581.0 eV (assigned to surface chromates) and a shoulder at about 578 eV (assigned to reduced chromium oxide clusters). After 30 minutes of calcination at 450°C the low binding energy shoulder has disappeared and the surface chromium peak has shifted towards 581.4 eV, indicating that the catalyst now features only chromate species anchored to the silica support. The surface area or the Cr 2p emission corresponds to 2.3 Cr/nm$^2$, implying that 1.7 Cr/nm$^2$ are no longer detected with XPS. Increasing the calcination temperature results in a further decrease of integrated Cr 2p intensity (figure 3.4) whereas peak shape and position remain unchanged.

The same peak shape and position are found for all sample measured in our experimental window (loading: 0.4 - 4 Cr/nm$^2$, calcination temperature: 450°C – 730°C) meaning that XPS detects only one type of anchored chromium on our model catalyst (figure 3.5). The apparent loading (determined from the integrated Cr 2p intensity) of series of catalysts with varying initial loading is plotted as a function of calcination temperature in (figure 3.6). While at high initial loadings the Cr 2p intensity decreases with increasing calcination temperature the Cr 2p intensity remains constant at low initial loadings. In our view the most probable explanation for these observations is that surface chromates can desorb from crowded silica surfaces and from the surfaces of chromium-oxide clusters.
Figure 3.5
Cr 2p spectra of model catalysts with different loading and calcination temperatures. Peak shape and position of the Cr 2p\textsubscript{3/2} maximum remain unchanged for all loadings (0.4 - 4.0 Cr/nm\textsuperscript{2}) and calcination temperatures (450\textdegree - 730\textdegree C). Within the sensitivity of XPS we are dealing with only one type of anchored chromate species.

Figure 3.6
The apparent chromium coverage decreases with increasing calcination temperature, however with low initial loadings the Cr coverage is much more stable with respect to high calcination temperatures. We assign the decrease in apparent Cr coverage to desorption of chromate, which happens most easily from crowded surfaces.
3.3.2. Rutherford Backscattering Spectroscopy RBS

Rutherford backscattering is used to clarify if chromium really desorbs from the silica support upon calcination, as it allows us to quantify the total amount of chromium on our model-catalyst regardless of dispersion. A model-catalyst wafer was loaded with 10 Cr/nm$^2$. One piece (1) was measured as prepared, a second (2) after calcination at 550°C. A third piece was placed parallel to a blank silica wafer (3) at about 1 mm distance and both were also calcined at 550°C. The RBS spectra shown in figure 3.7 show the hydrated (1), calcined (2) and the initially blank (3) silica wafer (top to bottom). Obviously the chromium-loaded wafer has lost some chromium through desorption. A large portion of the desorbed chromium is found on the blank silica wafer implying, that the chromium has a very high sticking probability. While the formation of volatile high valent oxides is common for molybdenum and tungsten, bulk CrO$_3$ is known to decompose to $\alpha$-Cr$_2$O$_3$ starting at 200°C even in oxygen atmosphere.

![Figure 3.7](image.png)

*Figure 3.7*  
RBS proves that chromate can indeed desorb from the model catalyst during thermal activation. A wafer with 10 Cr/nm$^2$ loading features 7.0 Cr/nm$^2$ after calcination at 550°C. The desorbing chromate readily readsorbs on an empty silica surface (labeled blank) placed opposite to the loaded wafer.
However calcination at higher temperatures leads to formation of mobile surface chromates (on the Cr$_2$O$_3$ cluster or crystallite surface) $^{[18,19]}$. When physical mixtures of bulk chromium compounds and empty support are calcined above 500°C surface chromate can be detected on the previously unloaded support$^{[20]}$.

While Jozwiek et al. $^{[20]}$ believe that redispersion of chromium on a support surface or from bulk oxide onto a support surface occurs via surface diffusion of surface wetting, Haber et al. $^{[21]}$ favor transport via gaseous CrO$_3$. It is still possible that surface diffusion plays an important role in the redispersion of chromium on silica, however, our experiments show unequivocally that transport through the gas phase is also significant.

### 3.3.3. Secondary Mass Spectrometry (SIMS)

SIMS was used to elucidate the structure of the surface chromate, which is anchored to the silica surface. Only this chromate is a precursor of the active site for ethylene polymerization as bulk chromium compounds fail to show any activity. Figure 3.8 shows the XPS and SIMS spectra of two model catalysts and a blank SiO$_2$/Si reference.

One catalyst has been prepared as the standard catalyst for our polymerization test: initial loading 2 Cr/nm$^2$, calcination at a maximum of 550°C in 20% oxygen/argon. The Cr 2p emission of the catalyst shows as expected only one signal for anchored chromate. The second catalyst has an initial loading of 4 Cr/nm$^2$ and is heated to 450°C in absence of oxygen. This pretreatment leads to a catalyst with both anchored chromate and reduced chromium as the loading exceeds the saturation coverage of the silica support.

The XPS spectrum shows a Cr 2p$^{3/2}$ peak at 581.4 eV of the surface chromate a pronounced shoulder at about 577.7 eV close to the 577.6 eV found by Merryfield et al $^{[14]}$ for highly dispersed chromium(III)-oxide on silica.

The negative- SIMS spectrum of the blank wafer (calcined at 550°C) (bottom) shows only two fragments at 136 and 196 amu which we assign to Si$_3$O$_5^-$ and Si$_5$O$_7^-$ respectively. The calcined catalyst (2 Cr/nm$^2$, O$_2$/Ar 550°C) show two additional fragments with mass 144 and 160 amu, we identify these as CrSiO$_4^-$ and CrSiO$_5^-$. The second catalyst (4 Cr/nm$^2$, Ar 450°C) shows again two additional fragments at 168 and 184 amu assigned as Cr$_2$O$_4^-$ and Cr$_2$O$_5^-$. The key observation is that the calcined catalyst, which features exclusively surface chromates, shows only Cr$_3$Si$_3$-fragments. Yet, on the second sample, where a part of the
chromium was forced to form clusters, Cr₂ fragments are easily detectable. In our view this is strong evidence that at all chromium coverages chromate can only anchor to the silica surface as a monomer. If dimeric species were formed on the silica surface they would have been detected with SIMS.

Figure 8. Cr 2p spectra and negative SIMS spectra of two model catalysts and a blank reference. The blank (bottom) shows only Si₃O₇ fragments, on a chromium loaded catalyst Cr₇O₅, fragments appear after thermal activation (Ar/O₂). If desorption of chromium is made impossible (in oxygen free argon) also Cr₂O₃ clusters can be detected. In combination this is strong evidence that chromate anchors to the silica surface as a monomer (see text).
3.4 Discussion

A CrO\textsubscript{x} / SiO\textsubscript{2} / Si(100) model catalyst prepared by spincoating impregnation from aqueous chromic acid has been studied using XPS, SIMS and RBS aiming at a molecular description of the calcination process of the Phillips catalyst. In many ways our model catalyst behaves as its industrial counterpart. Upon calcination the supported chromate form surface esters consuming surface hydroxyl groups of the silica support. The saturation coverage of chromate, which can be anchored to the silica support in such a fashion, depends on the amount of available surface hydroxyls decreases with calcination temperature. However, unlike on porous high surface area silicas we do not observe the transformation of excess chromate to Cr\textsubscript{2}O\textsubscript{3} at temperatures above 450°C on our model catalyst. Instead it desorbs from the silica surface (note that if a second surface is nearby – i.e. opposite to the original-most of the chromium will readсорb there). As a consequence calcination above 450°C produces catalysts exposing a silica surface, on which all chromium observed using XPS and SIMS is anchored to surface silanols. All Cr\textsubscript{2}O\textsubscript{3}-free catalyst showed the same Cr\textsubscript{2p\textsubscript{3/2}} binding energy at 581.4 eV, which we assigned to monochromate species, based on our SIMS findings.

![Figure 3.9](image_url)

*Figure 3.9.* After calcination at low temperatures (400°C) we observe a shoulder at 577.7 eV (Cr\textsubscript{2}O\textsubscript{3}-clusters) growing with increasing loading. Parallel to this the binding energy of the main chromium decreases significantly below 581.4 eV. The most straightforward explanation for this behavior is that a second surface chromate species with a binding energy around 580.5 eV appears, probably due to surface chromate on the Cr\textsubscript{2}O\textsubscript{3} particles (see also figure 3.3).
In earlier XPS experiments published in [22] we presented XPS data for a series model catalysts calcined at 400°C (figure 3.9). We observed anchored chromate at low loading. Upon increasing loading a shoulder at low binding energy grew which we assigned to Cr$_2$O$_3$-clusters. Parallel to the development of the Cr$_2$O$_3$-clusters we observed a downward shift of the “anchored chromate” signal. We explained this downward shift as a result of the superposition of two anchored chromate species, assigning them to mono (581.4 eV) and dichromate (580.6 eV) respectively. While we cannot completely rule out a silica-bound dichromate species after low temperature calcination (400°C), we believe now that the second chromate species is actually bound to the Cr$_2$O$_3$ surface. Prolonged calcination at 450°C leads to the disappearance of the Cr$_2$O$_3$ clusters and simultaneously to an upward shift of the “anchored chromate” peak towards its final value, 581.4 eV. Surface chromates on Cr$_2$O$_3$ might also explain other sighting of “anchored dichromate” in the literature like Weckhuysen et al. [6,23]. Table 1 summarizes all possible Cr species on SiO$_2$ after calcination.

Table 3.1: XPS (Cr 2p$_{3/2}$) binding energies of CrO$_x$ species on oxidic supports and in bulk compounds

<table>
<thead>
<tr>
<th>Entry</th>
<th>Support</th>
<th>Assignment</th>
<th>Binding Energy [eV]</th>
<th>S.O.S$^a$ [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>SiO$_2$/ Si[100] (calcined)</td>
<td>monochromate on SiO$_2$</td>
<td>581.4 ± 0.1</td>
<td>8.5</td>
</tr>
<tr>
<td>2</td>
<td>SiO$_2$/ Si[100] (calcined)</td>
<td>surface chromate on Cr$_2$O$_3$ cluster</td>
<td>580.5 ± 0.4</td>
<td>8.5</td>
</tr>
<tr>
<td>3</td>
<td>Cr$_2$O$_3$ cluster/ SiO$_2$/ Si [100]</td>
<td>Cr$_2$O$_3$ cluster/ SiO$_2$/ Si [100]</td>
<td>577.7 ± 0.2</td>
<td>9.1</td>
</tr>
<tr>
<td>4</td>
<td>SiO$_2$/ Si[100] (hydrated)</td>
<td>hydrated chromate / SiO$_2$</td>
<td>579.9 ± 0.2</td>
<td>8.9</td>
</tr>
<tr>
<td>5</td>
<td>Davison 952$^b$</td>
<td>Cr(VI)/silica (0.4 Cr/nm$^2$)</td>
<td>581.6 ± 0.3</td>
<td>9.0</td>
</tr>
<tr>
<td>6</td>
<td>Davison 952$^b$</td>
<td>Cr(III)/silica (0.4 Cr/nm$^2$)</td>
<td>577.6 ± 0.3</td>
<td>9.5</td>
</tr>
<tr>
<td>7</td>
<td>Al$_2$O$_3$$^c$</td>
<td>Cr(VI)/alumina</td>
<td>579.8</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>SnO$_2$$^d$</td>
<td>Cr(VI)/tin oxide</td>
<td>579.8</td>
<td>9.0</td>
</tr>
<tr>
<td>9</td>
<td>SnO$_2$$^d$</td>
<td>Cr(III)/tin oxide</td>
<td>576.6 ± 0.3</td>
<td>9.8</td>
</tr>
<tr>
<td>10</td>
<td>Davison 952$^b$</td>
<td>Cr(VI)/silica (0.4 Cr/nm$^2$)</td>
<td>581.6 ± 0.3</td>
<td>9.0</td>
</tr>
<tr>
<td>11</td>
<td>Davison 952$^b$</td>
<td>Cr(III)/silica (0.4 Cr/nm$^2$)</td>
<td>577.6 ± 0.3</td>
<td>9.5</td>
</tr>
<tr>
<td>12</td>
<td>Davison 952$^b$</td>
<td>Cr(VI)/alumina</td>
<td>579.8</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>Davison 952$^b$</td>
<td>Cr(VI)/tin oxide</td>
<td>579.8</td>
<td>9.0</td>
</tr>
<tr>
<td>14</td>
<td>Davison 952$^b$</td>
<td>Cr(III)/tin oxide</td>
<td>576.6 ± 0.3</td>
<td>9.8</td>
</tr>
</tbody>
</table>

$^a$ spin orbit splitting
$^b$ from ref [14]
$^c$ from ref [16]
$^d$ from ref [17]
The silica bound monochromate is the only detectable chromium species on our standard polymerization catalyst with an initial loading of 2 Cr/nm$^2$\textsuperscript{[11]} after calcination at 550°C (chromium coverage 1 Cr/nm$^2$). This catalyst shows a respectable catalytic activity while bulk chromium oxide is notoriously inactive for ethylene polymerization.

3.5 Conclusions

Studying the calcination behavior of chromium oxide supported on silica using a flat silica substrate and a combination of complementary surface science techniques is a powerful way to monitor the state of the supported chromium after calcination, the necessary pretreatment to activate the catalyst for ethylene polymerization. The model catalyst mimics the industrial Phillips catalyst closely enough to claim relevance; its starts out as a 2-dimensional aqueous solution of hydrated chromate that anchors to the silica surface consuming surface silanol groups. We profit from its defined surface and its conductivity. The most significant difference between surface science model and its high surface area match is the absence of pores or internal surface. This feature greatly facilitates the qualitative and quantitative interpretation of our data. However, if desorption and re-adsorption of the supported chromium come into play it will immediately disappear from the model catalyst, taken away by the gas stream, while on porous silica this process can obscured by readsorption. This will lead to differences between the surfaces of model and industrial catalysts, which have to be taken into account to avoid oversimplified extrapolations. On the other hand this also gives us an opportunity to look at desorption and readsorption as a mechanism for redispersion of the active phase on the silica surface or between support particles.

We indeed observe chromate desorption from the model catalyst, in particular at high Cr-loading (far above the nominal Cr-loading of the Phillips catalyst) and at high calcination temperatures. Chromate desorbs most easily from small chromium-oxide clusters and from crowded silica surfaces, while isolated surface chromates (on the silica surface) are stable during high temperature calcination. Inside the pores of a high surface-area silica gel the chromate can readily readsorb and will eventually produce new isolated surface chromate or more stable Cr$_2$O$_3$ crystallites. The silica bound chromate forming the active sites during ethylene polymerization assumes a monomeric structure.
Reference List

Ethylene polymerization with the flat CrO$_x$/SiO$_2$/Si(100) model catalyst

4.1. Introduction

Achieving realistic turnover on our flat CrO$_x$/SiO$_2$/Si(100) model catalyst has proven to be the most time consuming challenge of this project. Still, demonstrating realistic activity is of key importance to establish the validity of our model system for the industrial Phillips Catalyst.

The Phillips catalyst may be used in three different modes of polymerization namely the gas phase-, slurry- or solution process. These run at ethylene pressures between 15 and 30 bar and at temperatures between 65° and 180°C. With these processes more than 50 different types of polyethylene are produced, being either high-density polyethylene (HDPE), without long chain branching or, linear low-density polyethylene (LLDPE) incorporating various amounts of C$_4$-C$_8$ olefins.

For convenience we chose gas phase polymerization at 1 bar and 160°C in our first series of polymerization experiments. At this relatively high temperature we were expecting a high and constant polymerization activity as ethylene can activate (reduce) the surface chromate on the silica support without induction period[1].

As explained in chapter 2.2, model catalysts, which expose only about 1 square centimeter of active surface, are extremely sensitive towards minute amounts (ppm) of poisons in the gas feed. In our case the activated catalyst features at most one nanomol of chromium, hence 22 ml of gas feed containing 1 ppm of poison are enough to kill all catalytic activity within a few seconds (ethylene 5.0 may contain as much as 10 ppm water). We found a way around this problem using chromium-loaded alumina extrudates as a catalytic filter to clean the gas feed before it reaches the delicate model catalysts.
However, once we solved this technical problem we found that the catalyst became so active that it produced polymer films far too thick to be handled by surface science techniques - half a micron thickness represents an almost macroscopic dimension for a surface scientist. We had no way to “characterize” our polyethylene, which at that time meant: estimate the amount of material and prove that it consists of CH\textsubscript{2}. In addition we had vague ideas that AFM might become “interesting”. Consequently we turned to the polymer department for some advice as how to analyze these thin (thick) films.

This marked a turning point in this project as we soon began to realize that polymerizing on a flat substrate opens a somewhat different view on catalytic olefin polymerization as it offers excellent opportunities for the characterization of the polymer with techniques such as Scanning Force Microscopy (AFM). Apart from quantifying the polymer yield this technique gives detailed information about the morphology of the polyethylene as it has formed on the catalyst surface.

We choose to focus the last year of my thesis on exploring the possibilities of the flat model catalyst approach for studying catalytically formed polymer. We followed two major objectives, the intrinsic activity of polymerization (4.3) and the nascent morphology of polyolefins (5.3). We did not expect to learn anything new about the morphology of polyethylene as crystallized from the melt (4.4), which is supposed to be well-accepted textbook knowledge. However the observed morphologies where certainly spectacular and differed from what we expected when we looked at higher magnifications. These studies though not directly related to catalytic issues, have been tremendously useful to gain experience with this approach, establish confidence in it and demonstrate its feasibility.

4.2. **Experimental**

4.2.1. Preparation of the CrO\textsubscript{x}/SiO\textsubscript{2}/Si model-catalyst

The preparation of the CrO\textsubscript{x}/SiO\textsubscript{2}/Si model-catalyst by spincoating impregnation has been described in detail in section 2.2. Briefly, Si(100) silicon discs are calcined at 750°C for 24 hour to obtain a flat, amorphous silica layer of approximately 90 nm thickness. The silicon wafer is then cleaned in a mixture of concentrated hydrogen peroxide (30 volume %) and ammonia (30%) at 70°C. After further cleaning in boiling water the wafers are covered with the impregnation solution, chromic acid in water, and mounted on the spincoating device under nitrogen atmosphere. Upon spinning most of the solution is ejected from the
wafer leaving behind a thin evaporation layer. As the thickness of this layer can be calculated for any given rotation speed (here 2800 rpm), temperature (20°C) and solvent (water) \(^2\), the loading of the model catalyst can be controlled simply by varying the concentration of the (dilute) spin coating solution. For the polymerization studies reported here we chose an initial loadings between 2 Cr/nm\(^2\) and 200 Cr/µm\(^2\).

4.2.2. Ethylene polymerization reactor

Figure 4.1 shows the reactor used for the activation of the catalyst and the actual polymerization. It consists of two quartz tubes of 4 and 1 cm in diameter, respectively. The larger tube is surrounded by resistive heating cable and is sealed against atmosphere using viton o-rings on one side. The other side allows access to the thin tube and two gas valves, one connecting the reactor to a turbo-molecular pump, the other serving as gas exhaust during flow operation. The thin tube extends into the heated zone. Behind a quartz filter, the tube broadens into a holder, which may support up to 6 model catalysts. A chromel/alumel thermocouple, protected by a thin quartz tube, measures the temperature at this point. Before the quartz filter, upstream as seen from the model catalysts and within the heating zone, the thin tube is filled with γ-alumina extrudates impregnated with 0.17 wt% chromium (by incipient wetness impregnation from basic chromium(III) acetate solution). The chromium-loaded γ-alumina serves as a filter for the impurities in the ethylene feed stream.

*Figure 4.1*
Quartz reactor used for thermal activation of the CrO\(_x\) / SiO\(_2\) / Si(100) model catalyst and subsequent polymerization, details as described in text and in section 2.2
Before the reactor is loaded with the model catalyst, it is dried in vacuum to 200°C and subsequently baked out at 750°C in flowing O$_2$/Ar (20% O$_2$, dried with molsieves 4A), to remove water and sodium from the reactor walls. Next the model catalyst is inserted. After drying at 200°C in vacuum, the catalyst is calcined in flowing O$_2$/Ar at 550°C for 30 min (heating rate 20K/min, plateau at 450°C for 15 min). After cooling to 160°C the gas flow is stopped and the O$_2$/Ar is exchanged to argon (purified over a copper catalyst and a molecular sieve of 4A) and subsequently to ethylene. The gas exchange takes about 2 minutes, making the start time for the polymerization reaction uncertain to within at least one minute. Polymerization takes place in flowing ethylene at 160°C and at atmospheric pressure. Pumping away the ethylene and changing to argon atmosphere stops the reaction. The polyethylene formed on the catalyst surface is initially present as a molten film and is allowed to crystallize at 100°C for 2h before the reactor is cooled to room temperature.

4.2.3. Microscopy

Atomic force microscopy (AFM) images were taken on a Digital Instruments Dimension 3100 scanning microscope under ambient conditions. Measurements, performed in tapping mode (height images, amplitude or phase contrast as indicated on the images), were recorded by using etched Si$_3$N$_4$ tips (TESP) with a force constant of about 20-100 N/m. Polyethylene layer thickness was determined using the height difference between the Si-substrate and the polyethylene surface after scratching the layer with a scalpel. The thickness measurement of the polyethylene film was controlled with two independent techniques namely Rutherford Backscattering Spectrometry (RBS) and Scanning Electron Microscopy (SEM).

4.2.4. Rutherford backscattering Spectrometry

RBS spectra were measured with an incident beam of 4 MeV He$^+$, produced with the AVF-cyclotron at the Eindhoven University of Technology \cite{3}. Det2ails concerning beam optics and detectors have been published elsewhere \cite{4}. The overall energy resolution was measured to be 18 keV. We adopted a scattering geometry with the incoming beam directed along the surface normal and a scattering angle of 170°. As scattering of He$^+$ at 4 MeV off carbon and oxygen is non-Rutherford like, we used scattering cross-section data measured at a scattering angle of 170.5° for carbon \cite{5} and at 170° for oxygen \cite{6}. We assume that the cross-sections are accurate within 5%.
4.3. **Activity and Stability**

4.3.1. What kind of polymer do we produce?

If a calcined model catalyst is treated with atmospheric ethylene at 160°C, it immediately develops polymer, which forms a thin, molten film visible to the eye by Newton colors. Obviously this polymer is polyethylene, however, the exact type of polyethylene is uncertain.

The catalytic performance of the Phillips catalyst and the properties of the polymer product are very sensitive towards the exact recipe of the catalyst and the mode of polymerization. Even if pure ethylene is used as feedstock the produced polyethylene may vary in molecular weight and in molecular weight distribution. Side reactions during chain growths may induce methyl- or even long chain branching.

![Scheme 4.1 Methyl branching](image1)

![Scheme 4.2 Long chain branching](image2)
These reaction are very slow compared to the normal insertion of ethylene. However even minute amounts of these side branches can have an enormous influence on the polymer properties e.g. on its crystallinity. The probability for chain branching is again dependent on the polymerization parameters. While insertion of a monomer is first order in monomer concentration, the termination reaction ($\beta$-H elimination) and chain branching are independent of the ethylene concentration. Especially methyl branching becomes more common if the polymerization is carried out at atmospheric pressure or less\textsuperscript{[1]}. Evidently it is very desirable to study the primary structure of the polymer particles as it determines the quality of the produced polymer and it reflects an essential part of the catalyst reactivity.

![Figure 4.2](image)

**Figure 4.2**

ATR-IR spectra of branched LDPE (top), linear HDPE (middle) and PE as produced on the CrO\textsubscript{x}/SiO\textsubscript{2}/Si(100) model catalyst (160°C, 1 atm C\textsubscript{2}H\textsubscript{4}, 1h, 420 nm, bottom). Our polymer features the sharpest bands both in the CH stretching region ($\nu$(CH\textsubscript{2}), left) and in the CH\textsubscript{2} bending region ($\delta$(CH\textsubscript{3}), right). The broad shoulder between 1425 and 1450 cm\textsuperscript{-1} that is most pronounced in LDPE is indicative for the amorphous part in the polymer. It is almost undetectable in the spectrum of the polymer produced on the flat model catalyst indicating that it is highly crystalline.
Unfortunately our possibilities with regard to this aspect are very limited: standard techniques to determine the molecular weight distribution or the amount of methyl groups in the polymer chains ($^{13}$C-NMR) require at least hundred milligrams of material. We need at least a factor of 1000 higher catalytic yield than we have achieved with our current experimental setup.

We expect that the high polymerization temperature (160°C) in combination with the low polymerization pressure (1 atm) results in relatively short chains with a molecular weight in the order of 10,000 amu and a considerable amount of methyl branching.

On the other hand infrared spectroscopy, which can be performed in attenuated total reflection ATR mode using a Golden Gate accessory spectrometer, shows no sign of methyl groups in the polyethylene produced on the CrO$_x$ / SiO$_2$ / Si (100) model catalyst Figure 4.2. Furthermore the extremely sharp IR-bands plus the absence of the amorphous part in the $\delta$(CH$_2$) band indicate that the polyethylene produced on the flat silica wafer is highly crystalline and that the amount of branching is small.

4.3.2. How to determine polymerization activity on the flat CrO$_x$ / SiO$_2$ / Si(100) model catalyst

After the desired polymerization time the ethylene is pumped away and the reactor is cooled slowly to 100°C (arbitrarily chosen) for two hours to allow crystallization of the polyethylene film. The PE thickness has been determined using three independent methods, giving consistent results figure 4.3:

- Analyzing scalpel scratches on the silicon wafer with AFM indicating thickness of up to 400 nm.
- After partially lifting of the polyethylene film using trichlorethane, the film could be imaged with SEM. The film formed during 60 min of polymerization measures 400 nm in thickness.
- While the first two methods are local in nature, the RBS spectra of figure 4.3 bottom yield the average thickness over the area of the beam (2 mm in diameter). The symmetrical carbon peak at the two short polymerization times indicates a homogeneous layer thickness, whereas the tailing observed after 30 minutes of polymerization may be interpreted as a result of a larger variety of film thickness at
this stage. The spectra show a broad continuum below 2.3 MeV due to the silicon substrate, a peak at 1.45 MeV attributed to oxygen originating from the SiO\textsubscript{2} layer of the model catalyst and a peak at 1.015 MeV attributed to carbon from the polyethylene overlayer. The amount of carbon on the samples has been calculated by evaluating the ratio of the integrated C peak and the height of the silicon continuum. The polyethylene overlayer was taken to have a stoechiometric composition of CH\textsubscript{2}, resulting in areal densities of 0.8x10\textsuperscript{18}, 1.3x10\textsuperscript{18} and 2.75x10\textsuperscript{18} CH\textsubscript{2}-units/cm\textsuperscript{2} for the samples after 10, 15 and 30 min of reaction, respectively.

Figure 4.3
SEM, AFM and RBS are used to determine the thickness of the polymer film produced by the CrO\textsubscript{x} / SiO\textsubscript{2} / Si(100) model catalyst. For details see text.
This corresponds to polyethylene layers of 68, 110 and 232 nm thickness, respectively, when the density of the formed polyethylene is taken as 0.92 g/cm$^3$. Simulations of the carbon peak shape [20] suggest variations of about 18% in the thickness of the 232-nm polyethylene layer. These variations in height are associated with the beginning of spherulite growth, as described in section 4.4.1.

4.3.3. How active is the model catalyst?

Despite of some scatter in the data, the thickness of the catalytically grown polyethylene film clearly shows a linear correlation with polymerization time, indicating a constant polymerization rate for at least the first hour of reaction. All the chromium on the flat silica support is molecularly dispersed and anchored to the surface [7,8] and is equally accessible for the ethylene. In addition the catalytically active surface remains constant during polymerization, which is not necessarily true for porous supports that fracture during polymerization. Assuming all chromium atoms equally active we extract a pseudo-turnover frequency of 2.5 s$^{-1}$ (molecules ethylene per atom chrome and second).

Translated to a high surface area CrOx/SiO$_2$ catalyst from Crossfield (286 m$^2$/g), the activity corresponds to 120 gram of polyethylene per gram of catalyst and per hour at 1 bar total pressure. An industrial catalyst calcined at 500°C produces about 1 kg of polyethylene per gram of catalyst per hour, however, in a butene slurry at 105°C, a total pressure of about 40 bar and an ethylene partial pressure of about 15 bar [1,9,10]. Szymura et al [11] report a polymer yield of 25.5 g(PE) / g(catalyst) for a Crossfield silica loaded with 5 wt% Cr, during polymerization at 25°C and atmospheric pressure in a hexane slurry, over a CO-prereduced catalyst. While the precise values are difficult to compare due to differences in catalyst preparation, reaction conditions and the fracturing of the industrial catalyst, we conclude that the model catalyst displays a polymerization activity in the same order of magnitude as its industrial counterparts.

The polymerization activity of the industrial Phillips catalyst is very sensitive towards the calcination temperature. While the anchoring of the chromate species is complete at 450°C and XPS finds no clue for a further change in the chromate environment (3.3), the increase in activity is usually attributed to a further decrease of surface-hydroxyl density upon increasing the calcination temperature. The surface hydroxyls are thought to interfere with the polymerization reaction. While this sounds plausible, to our knowledge no direct evidence for this hypothesis exists in the literature (see also 5.1.3.).
Figure 4.4 (left) shows the polymer yield versus the polymerization time for three model catalysts. They all have an initial loading of 2 Cr/nm² but have been activated at different temperatures. The polymerization activity increases with increasing calcination temperature, just as in the industrial Phillips catalyst.

**Figure 4.4**
The polymer yield (in nm film thickness) shows a linear correlation with polymerization time for a series of CrOₓ/SiO₂/Si(100) model catalysts with 2 Cr/nm² and varying calcination temperature. The polymerization takes place at 160°C in 1 atm ethylene. The catalytic activity is constant during the first hour of polymerization and increases with calcination temperature. The values on the right plot are from scalpel scratches analysed by AFM.
Table 4.1. Catalytic activity of the CrO$_x$/SiO$_2$/Si(100) model catalyst for ethylene polymerization at 160°C and 1 bar of ethylene

<table>
<thead>
<tr>
<th>$T_c$ $^a$</th>
<th>coverage $^b$</th>
<th>Catalytic activity</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[°C]</td>
<td>[Cr/nm$^2$]</td>
<td>[nm (PE) / min]</td>
</tr>
<tr>
<td>450</td>
<td>2</td>
<td>2.2 ± 0.4</td>
<td>0.4</td>
</tr>
<tr>
<td>550</td>
<td>1</td>
<td>7.4 ± 0.2</td>
<td>2.5</td>
</tr>
<tr>
<td>650</td>
<td>1</td>
<td>10.7 ± 0.3</td>
<td>3.7</td>
</tr>
</tbody>
</table>

$^a$) calcination temperature [thermal activation in O$_2$/Ar (20/80)]

$^b$) during calcination a portion of the catalyst loading desorbs

$^c$) pseudo turn over frequency assuming all Cr is active

$^d$) for a silica support with 286 m$^2$/g (Crossfield)

4.4. Morphology of polyethylene crystallized from the melt

Depending on the polymerization time we observe different morphologies of the polymer film, which reflects the increasing layer thickness of the molten film. In the first 2 minutes of the experiment oxygen is replaced ethylene. The reactor is evacuated three times and subsequently it is flushed with ethylene. Simultaneously the catalyst is reduced by ethylene and begins to polymerize. Depending on the polymerization time (vis film thickness) the polymer develops different morphologies which are shown in Figure 4.5 and 4.6 at different magnification. During the transition period the catalyst produces mainly low molecular weight parafins (3 min). After 5 minutes we see a closed film of polymer with two morphological features. Most of the surface is covered with a plate like morphology, which features sharp and straight domain boundaries. We assign this region to a closed layer of stacked lamella crystals growing edge-on on the silica substrate (see section 4.4.2). Besides these edge-on lamellas we observe sheaf-like, curved structures growing on top of the first layer, starting from a nucleation center. This sheaf-like layer (also orientated edge-on with respect to the silica surface) becomes more prominent after 10 minutes and forms an almost closed layer after 15 minutes. However, when this layer is completely filled the polymer starts to grow in the third dimension, grain boundaries appear after 30 minutes between 2 dimensional spherulites (see 4.4.1) of approximately 50 µm in diameter. The average film thickness is on the order of 250 nm. Closer examination reveals that all spherulites contain pronounced nucleation centers from which lamellae grow sheaf-like.
Figure 4.5
Surface morphology of PE films produced on CrO₃/ SiO₂/ Si(100). C₂H₄ (1bar), 160°C
Figure 4.16
Surface morphology of PE films produced on CrO$_x$/SiO$_2$/Si(100). C$_2$H$_4$ (1 bar), 160°C
Adjacent to the center of the spherulites, circular regions appear. These depressed regions show a plate-like morphology of the underlying layer. After 60 minutes of ethylene polymerization the average layer thickness is about 420 nm. The nucleation centers, though clearly recognizable, have been covered by a dome-like structure of polyethylene lamellar crystals. The bright contrast of the center and the distinct spherulite boundary are indicative of a 3-dimensional spherulite, as is confirmed by optical polarization microscopy not shown).

4.4.1. Lamella crystals and development of spherulites

Spherulites are a well-known superstructure of lamella crystals that form when polyethylene is crystallized from the melt. We can observe different stages in the development of these spherulites as the thin films offer only a limited amount of material.

Lamella crystals (figure 4.7) consist of folded chains of polymer that align parallel to each other to form a plate-shaped crystal, which can extend several micrometers. The thickness of the lamella crystal is dependent on the crystallization temperature and is in the order of a few tens of nanometers. It is a sandwich structure with the crystalline part in the middle consisting of polyethylene segments aligned parallel to each other. The bended regions of the chains make up the amorphous part of the solid polymer, which also contains polymer chains or segments thereof which are not incorporated in the crystalline part of the lamella. The crystallinity (portion of the polymer chains in the crystalline part in parallel alignment to each other) can be estimated for polyethylene from IR or Raman spectra.

Spherulites (Figure 4.8) are the result of a sheaf-like growth of folded chain crystals, starting from a nucleation center. In bulk polyethylene they grow in three dimensions, while with our thin films we also observe a two-dimensional growth.

We can conclude at this point that AFM has delivered a series of beautiful pictures of the polyethylene produced on our model catalyst. The “polyethylene” that we produce with the CrO_4 / SiO_2 / Si(100) model at high temperature and low pressure is well behaved. It features CH_2- chains, long enough to crystallize, as polyethylene should.

4.4.2. Edge on lamella crystals in closed films

Before the sheaf like growth of the lamella crystals that leads to the development of the spherulite aggregates is observed the silica wafer is covered with lamella crystals growing
in edge-on orientation with respect to the substrate. Figure 4.9 shows the surface morphology of such a film in height, amplitude and phase contrast. The height variation on the 20*20 µm² area is about 10 nm. While all imaging modes show the same morphology, phase and amplitude mode show more detail in the stacking of the lamella crystalls. They are aligned parallel to each other in domains of a few square micrometers. These domains are induced by pronounced edge-on lamellae with a length of several micrometers. A similar morphology has been observed in transmission electron microscopy studies on thin cast-films of isotactic and syndiotactic polystyrene \(^{[12,13]}\).

![Diagram of lamella crystal](image)

*Figure 4.7*

Top view of two idealized folded chain crystal (lamella crystal) growing edge-on on a flat substrate (gray rectangle). Lamella crystals are semi-crystalline: the ordered (crystalline) part consists of segments of polymer chains in all-trans conformation (in the direction of c), which are stacked in parallel alignment. The folded regions of polymer chains make up the amorphous part, which also accommodates regions of the polymer-chain, which are not incorporated in the crystalline part (e.g. long branches). The main direction of growth is horizontal (in the direction of b) and a PE-lamella can extend up to a few µm. The width of lamella crystals (vertical, in the direction of c) varies with crystallization temperature and is in the order of a few tens of nanometer.
Folded chain crystals start to grow in a linear fashion, starting at a nucleation center (small dot). Mistakes during crystal growth lead to nucleation of secondary lamellae, which are forced to bend away until the growing arms meet each other. A pair of circular regions adjacent to the center of the spherulites remains empty as this two-dimensional spherulite ran out of material. Crystallization stopped before the spherulite was completed.

On a fully grown 3-dimensional spherulite the nucleation center remains visible, while the boundaries between spherulites become more distinct. At higher magnification we observe, how folded chain crystals (now growing in two dimensions) assemble to form the spherulite aggregate.
Figure 4.9: AFM images of the polyethylene surface morphology recorded in height, amplitude and phase contrast. Scan size is 20 by 20 μm² and height variation from dark to bright areas is 20 nm. The solid square marks the position of figure 4.10-a.
We observe more details of the morphology of lamellae agglomerations and their interaction with other domains at higher magnification. Using phase contrast mode and a scan size of 4 by 4 µm² several domains with parallel-aligned lamellar crystals are clearly separated (Fig. 4.10-a,b).

![Image](image_url)

**Figure 4.10**
AFM images of the polyethylene surface morphology recorded in height (a, contrast 30 nm) and phase contrast (b,d). Scheme (c) depicts the domain boundaries and the orientation of the stacked lamella crystals in (a,b); in some regions (dotted areas) situated at the domain boundaries no lamella crystals can be resolved. Especially in the high magnification phase image (d) we observe a grainy sub-morphology in the edge on lamella crystals (solid square marks the position of (d) in (a-c), broken square in (d) marks position of 4.11).
The domains are nonuniform in size and the lamellae have a thickness of approximately 30 nm. Because of the tip-sample interaction this 30 nm thickness is the sum of both, the thickness of the crystalline and of the amorphous phase, and should be compared only with repeat periodicity data from small angle X-ray scattering investigations. Next to edge-on lamellar crystals, some regions of Fig. 4.10 exhibit crystals with different shape: here, accumulated crystals have a low aspect ratio of almost one. The corresponding sketch (Fig. 4.10-c) indicates the main localization of these regions. The crystals with low aspect ratio are present especially at the boundaries between two regions with parallel edge-on lamellae. Because of their location at the boundaries and their smaller size compared to the thickness of the edge-on lamellae, we assume that these parts were formed towards the end of the crystallization.

Further increase of the magnification yields more details in the architecture of the domains formed by edge-on lamellae and their boundaries. The phase mode image with a scan size of 1 by 1 µm$^2$ (Figure 4.10-d) shows a uniform grainy sub-morphology of the lamellae. A similar grainy morphology is observed for polyethylene copolymers and for syndiotactic polypropylene$^{[14,15]}$. In phase-mode images the contrast is caused by the different phase lag of the cantilever for the crystalline core (stiff) and the amorphous layers (soft) of folded chain crystal. An additional phase lag variations inside the crystalline part of the lamella gives rise to the grainy sub-morphology$^{[16]}$. A phase image similar to the observed one in Fig. 4.10-d may also be caused by small cracks at the surface, formed during cooling and possibly initiated by local surface tension during crystallization. We stress, however, that especially in the height images we do not find any indications for cracks at the surface of the investigated samples.

Fig. 4.11 shows a set of three AFM images using height, amplitude and phase contrast at a scan size of 400 by 400 nm$^2$. All three images show similar details of the lamellae sub-morphology. Blocks having a thickness-to-width ratio of approximately 3:2 form the lamellae, e.g. the block marked in Fig. 3c with a thickness of 32 nm and a width of 21 nm. The lamellar crystals are distinctly separated from other lamellae, whereas the block boundaries inside the crystal are less pronounced. For optimized scanning conditions the height contrast yields additional information of the origin of the grainy sub-morphology. In addition to height variations in the order of 2 nm between the crystalline core of the lamellae and the surrounding amorphous layers we observe small height variations (about 1 nm) between the blocks and the block/block interfaces in a single lamellar crystal.
AFM images of the polyethylene surface morphology recorded in height, amplitude and phase contrast (left to right). Height variation from dark to bright areas is 10 nm in Fig. 3a and the arrow in Fig. 3c indicates a grainy block measured for discussion. The schematic representation on the bottom shows the stacking of the building blocks which align with a guiding lamella crystal; individual lines represent segments of the polyethylene chain.
These finding are not consistent with the established “two phase model” for folded chain crystalls of polyethylene \cite{17,18} (see Fig 4.7) that predicts a homogeneous crystalline part (segments of the polymer chain in parallel alignment) that extends over the entire crystal (a few \( \mu \text{m} \)). Assuming that during the polymerization a molten PE film with homogeneous thickness is formed, our experimental data indicate the existence of third phase in the polyethylene lamellas produced by the CrO
\[\text{CrO}_x/\text{SiO}_2/\text{Si}(100)\] model catalyst.

Beside the crystalline core with high density (phase I) and the amorphous phase with relative low density (phase II) the three phase model introduces a less organized interphase of intermediate density (phase III) \cite{19,20}. After crystallization of the polymer; the height variation between the lamellar core and the amorphous layers reflect the differences in final density of these phases (phase I and II). The slight height differences between the grainy blocks and the block/block interfaces should be assigned to a less organized interphase (phase III) with intermediate density. The phase contrast image (Fig. 4.11) reflects the same density variations. The reason why we can observe the grainy substructure of our melt crystallized polyethylene lamella crystals is that they are orientated in perfect edge-on orientation; so we can obtain a side view. This facilitates the use of AFM in phase contrast with its high sensitivity to material properties (softness). A tentative interpretation of the observed building blocks is that preforms of these blocks exist already in the supercooled melt. These precursors align with the first lamella crystals that crystallize, build up in decreasing order with increasing distance to these guiding lamellas. As the lamella precursors do not match perfectly in orientation a less organized interphase forms between the building blocks upon crystallization. If the ordering or the building blocks becomes too low – at domain boundaries- the lamella crystals do not grow.

In summary, the CrO
\[\text{CrO}_x/\text{SiO}_2/\text{Si}(100)\] model catalyst produces well defined, thin polyethylene films, which are ideal for the study of the surface morphology using AFM. These images reveal an unexpected substructure in the crystalline part of edge-on grown lamellar crystal. This preliminary data is supporting evidence for a recently proposed and at this moment somewhat controversial three-phase model for lamellar crystal growth. A systematic study of these polymer films under more defined crystallization conditions offers a way to improve our understanding of the crystallization behavior of polyolefins.
4.5. Ethylene polymerization at low Cr-loading – isolated active sites

As an alternative to control the polymer thickness by simply varying the polymerization time, one can also vary the chromium loading at constant polymerization time. As expected, we observe the same morphologies as discussed in the previous sections (lamella crystals growing edge-on or sheaf-like, not shown).

At 2000 Cr/µm (a factor of 1000 below the normal 2 Cr/nm used for most polymerization experiments) the polymer film produced after one hour of polymerization at 160°C is only a few nm thick but still closed (figure 4.12 left). With AFM we do not observe any lamella crystals in these films, probably because they are simply too thin to form a crystalline polyethylene phase. Increasing the distance between active sites by decreasing the catalyst loading another order of magnitude leads to a situation where the polymer film no longer forms a closed layer but breaks up into isolated islands (figure 4.12 right).

Such isolated polymer islands have indeed been prepared. Figure 4.13 shows a catalyst with a nominal loading of 200 Cr/µm² (left) as compared to a blank reference (right). Both samples were calcined at 550°C and then treated with 1 bar of ethylene at 160°C for 1h. The chromium-loaded sample contains at least 70 particles in an area of 1*1 µm² with a threshold height higher than 1.2 nm, whereas the blank (i.e. chromium-free) reference surface features none. Two particles are substantially larger than the others, especially in

![Cr loading 2000 / μm² closed PE-layer](image1.png) ![Cr loading 200 / μm² PE islands 70 / μm²](image2.png)

*Figure 4.12*
AFM-image (amplitude contrast) of polyethylene produced on the CrOₓ/ SiOₓ/ Si(100) model catalyst at 160°C and 1 atm C₂H₄. Cr coverage of 2000 Cr/µm² yields a closed layer of polyethylene, while 200 Cr/µm² give isolated polymer islands.
height, and these are non-spherical in shape. We assign these to polymer that has been produced by several active sites. The large majority, however, appears to have spherical shape with an average height of about 2 – 3 nm. We assign these particles to polymer that has been produced by isolated active sites, which are sufficiently separated to prevent coagulation. While it is generally accepted that the active sites of the Phillips catalyst are molecularly dispersed, it is still possible that the active site consists of two or even three chromium atoms, since the area of 1x1 µm$^2$ in figure 4.13 contains 70 polymer particles and 200 Cr-ions. However, SIMS and XPS analysis strongly suggests that the chromium is exclusively present in the form of monochromate after calcination (section 3.3.3).

Figure 4.13
AFM image (1 x1 µm$^2$, height contrast, topview and sideview) of two model-catalysts after polymerization (160°C, 1h). Left: loading 200 Cr/µm$^2$ resulting in at least 70 PE islands of at least 1.5 nm in height. Right: blanc reference with average roughness of 0.5 nm without any island higher than 1 nm. The arrow marks the polymer island discussed in Figure 4.14.
We can use AFM to estimate the catalytic activity of the individual active sites on the CrO$_x$/SiO$_2$/Si(100) model catalyst as illustrated in figure 4.14. The AFM tip with a tip-radius of 5 nm overestimates the particle diameter by only 1-2 nm (section 2.2.2). Assuming the polymer island in Figure 4.14 has been produced by an isolated active site bearing one chromium atom, we calculate the turnover frequency of this site to be $17 \pm 2 \text{ C}_2\text{H}_4/(\text{Cr}^*\text{s})$. The polymer island in this example is relatively big, the average turnover frequency determined from 25 polymer islands on figure 4.13 results in $6.6 \text{ C}_2\text{H}_4/(\text{Cr}^*\text{s})$, again assuming that they are the product of isolated chromium sites. Acknowledging that we only have a few successful polymerization runs in the isolated active site regime we refrain from drawing any simple minded conclusions at this point. It is difficult to judge how far deactivation of some of the active sites or coalescence of some of the isolated polymer islands corrupt the information about the catalytic activity that can be deduced from these pictures. Nevertheless we conclude that is possible to produce and visualize isolated polymerization sites on the CrO$_x$/SiO$_2$/Si(100) model catalyst using AFM and that we can even quantify their catalytic yield. The concept of isolated polymerization sites has been proven.

**Figure 4.14**
Electronic zoom of the polymer island marked in figure 4.13. The particle has paraboloid shape, with a diameter of 48 ± 2 nm and a height of 3.1 ± 0.1 nm. This corresponds to a volume of about 2800 nm$^3$. Assuming that the polymer has been produced by a single active site, we calculate its activity (average turnover frequency over the 1 hour polymerization run) to be $17 \pm 2$ molecules (C$_2$H$_4$) per chromium atom and second. The AFM tip shown for comparison is of paraboloid shape and has a tip radius of 5 nm.
A systematic study of the low loading regime (varying both chromium loading and polymerization time) should be able to resolve some very fundamental questions about the activity of the Phillips catalyst e.g. how does activity develop in time, how many chromium sites take part in the catalytic reaction, is there a activity distribution?

4.6. Conclusions

In the previous examples we have demonstrated that ethylene polymerization on the CrO$_x$/SiO$_2$/Si (100) model catalyst is possible and produces polymer films of up to half a micrometer thickness corresponding to a yield of 0.1 mg. The catalytic activity of the CrO$_x$/SiO$_2$/Si (100) model catalyst per unit surface area is about the same as the activity of the industrial catalyst and no poisoning of the catalyst is observed even though the small amount of active sites make our catalyst very demanding with regard to purity of the gas feed.

While the catalytic yield is still about a factor 1000 below the amount needed to do a common chemical characterization ($M_w$, $M_m/M_n$, NMR) of the polymer chains, the crystallization behavior and the IR-spectra indicate that we indeed produce linear polyethylene with an undetectable amount of side branches.

The thin polymer films produced on the flat support are ideal for morphological studies using scanning force microscopy, as the polymerization takes place at 160°C, the observed films are as crystallized from the melt. Ultra-thin (a few ten nm) films of polyethylene with low roughness, which are difficult to produce by more conventional preparation techniques (e.g. spin coating) have been prepared by this technique. They show stacked lamella crystals in perfect edge-on orientation. A combination of height and phase contrast (AFM) reveals a grainy sub-morphology lamella crystals, which can be imaged in nanometer detail. Finally we demonstrated that it is possible to image isolated polymerization sites and even to estimate their catalytic activity one by one.
Reference List

16. Application notes, Digital Instruments Inc. (Santa Barbara, California , , 1999)
Concluding remarks and Outlook

5.1. The flat model catalyst approach and the Phillips catalyst

If I was forced to state the essence of this thesis in only a few words I would probably say that we have been using the CrO₅ / SiO₂ / Si(100) system as a test case in exploring the possibilities and limits of the flat model catalyst approach. In the beginning we focussed on the preparation of the model catalyst resembling the industrial preparation of the Phillips ethylene polymerization catalyst as close as possible. In the first stage of the preparation chromium is impregnated on the flat silica support by spincoating aqueous chromic acid on a silicon wafer. This methods imitates pore volume impregnation used with conventional silica gels and yields homogeneously dispersed chromate with full control over the catalyst loading.

We followed the molecular state of the supported chromium during thermal activation (calcination) of the catalyst in dry Ar/O₂ using a combination of X-ray photoelectron spectroscopy (XPS), secondary ion mass spectrometry (SIMS) and Rutherford backscattering spectrometry (RBS). The major advantage of a thin-film (up to 90 nm) and flat silica support is that the surface probed by our spectroscopies is identical with the catalytic active surface. This greatly facilitates the qualitative and quantitative interpretation of our data.

5.1.1. How realistic is the CrO₅ / SiO₂ / Si(100) model catalyst?

In agreement with the established picture of the industrial Phillips catalyst, we observe molecularly dispersed chromate ions that are embedded in a water matrix after spincoating impregnation. Upon calcination this chromate anchors to the silica support forming chromate esters with the surface silanol groups of the support. The maximum amount of anchored surface chromate is limited by the amount of surface silanol groups and decreases
with increasing calcination temperature. At low calcination temperatures (450°C) 2.3 Cr/nm$^2$ have been detected on the CrO$_x$ / SiO$_2$ / Si(100) model catalyst, exclusively in the surface chromate state. This is in exact agreement with saturation coverage measurements done on the industrial Davidson 952 silica, which is fully hydroxylized (about 5 OH/nm$^2$).

On porous silica supports the superficial chromium that cannot be anchored to the silica surface is transformed to the thermodynamic most stable chromium oxide Cr$_2$O$_3$, which depending on the amount forms small clusters or even crystallites. On our flat CrO$_x$ / SiO$_2$ / Si(100) catalyst, however, we observe a different behavior. Regardless of initial loading or calcination temperature we find exclusively monochromates on the flat silica support. The superficial chromium desorbs from the surface and is taken away with the gas flow. If another silica surface is nearby, as in the pores of a silica gel or if second wafer is placed opposite to the chromium loaded silica surface, the chromate readily re-adsorbs on this surface. The industrial Phillips catalyst work with an average chromium loadings below 0.4 Cr/nm$^2$, while we observe that flat model catalysts with a chromium loading below 1 Cr/nm$^2$ are stable against chromium loss through desorption up to the highest calcination temperature in our experiments, 730°C. Still Cr-desorption can act as a mechanism to isolate the anchored chromium and thus to remove locally high concentration of active phase.

Most important for the validity of the Phillips model catalyst is unquestionably the catalytic activity for ethylene polymerization. In our view the CrO$_x$ / SiO$_2$ / Si(100) catalyst has passed this ultimate test quite strikingly (chapter 4). In conclusion we believe that the flat CrO$_x$ / SiO$_2$ / Si(100) system is indeed a realistic model for the Phillips ethylene polymerization catalyst. It shows essentially the same surface chemistry as its industrial counterpart, namely a molecular dispersed chromate that is anchored to the silica support after thermal activation and a decent catalytic activity that increases with increasing calcination temperature. Of course it is not a one on one image of the real catalyst, because we have removed its porosity. This simplification enables us to draw more conclusions out of the surface science characterization and do it with more confidence.

5.1.2. What have we learned about the thermal activation of the CrO$_x$ / SiO$_2$ / Si(100) model catalyst?

The most prominent result of our calcination study of the CrO$_x$/SiO$_2$ system was that chromate anchors to the silica surface exclusively as monochromate-ester independent of
calcination temperature or initial chromium loading. This observation is in contradiction with the generally held view that high calcination temperature and high chromium loading induce surface dichromates. On porous supports under these conditions also Cr$_2$O$_3$ clusters may form, which also feature surface chromates or dichromates$^{[1,2]}$ and are (almost) inactive for ethylene polymerization$^3$. If both surfaces (SiO$_2$ and Cr$_2$O$_3$) are present simultaneously an assignment of the surface chromate species to the silica surface is not valid. We believe that the spectroscopic sightings of “surface dichromates or even polychromates”$^{[4,5]}$ on calcined silicas are in fact due to the formation of surface chromates on small Cr$_2$O$_3$-clusters.

On the CrO$_x$/SiO$_2$/Si(100) model catalyst, however, we observe only the silica bound chromates as the superficial chromium desorbs from the surface. This leaves us with somewhat boring XPS spectra (see figure 4.4 and 4.5) showing only one chromate species regardless of calcination temperature or initial loading. Even under the most crowded condition (highest surface chromate coverage) we find only evidence for the existence of silica bound monochromates in the SIMS spectra.

The calcined model catalysts are active for ethylene polymerization if the temperature is high enough to allow the reduction of the surface chromates in the ethylene stream. At 160°C this reduction very fast and the catalyst shows a constant polymerization activity. The activity increases with increasing calcination temperature, which is the expected behavior of the Phillips catalyst. We find no correlation between the activity and our XPS data as the binding energy of the Cr 2p emission remains unchanged with varying calcination temperature. The increase of polymerization activity of the Phillips catalyst upon increasing the calcination temperature is usually attributed to a decrease of hydroxyl population on the silica surface. The most generally held view is that surface hydroxyls decrease the coordination unsaturation of the active site and thus decrease the catalytic activity. The interaction between supported chromium and surface hydroxyls and the coordination unsaturation of the supported chromium have been investigated using CO reduced CrO$_x$/SiO$_2$ catalysts. Unfortunately we were not able to study CO reduced CrO$_x$/SiO$_2$/Si(100) catalysts because the reduced chromium quickly reoxidized in the preparation chamber (see section 2.2). While we stopped our efforts to produce a CO reduced CrO$_x$/SiO$_2$/Si(100) catalyst within the scope of this thesis we still think that a surface science study of this system could make a great contribution towards a better understanding of the Phillips catalyst.
5.1.3. The CO-reduced Phillips catalyst

If ethylene is polymerized over a calcined CrO\(_x\)/SiO\(_2\) catalyst at temperatures around 100°C no polymerization takes place during the first few minutes of reaction. During this induction period the supported chromate is reduced by ethylene to form the active species.

Alternatively the surface chromate can be reduced by other reducing agents like alkyls of aluminum, boron or zinc or carbon monoxide, which all eliminate the induction period. Catalysts that are prereduced by carbon monoxide even show catalytic activity at room temperature and below, while the calcined catalysts show no activity below 60°C \[^3\]. Thus the reduced chromium resembles the active site closer than surface chromate and consequently has received a lot of attention.

Krauss and Stach \[^6\] found that at 350°C, CO quantitatively reduces surface chromates to chromium(II), which is believed to be the active valence of the Phillips catalyst. The supported chromium is highly coordinatively unsaturated adsorbs a number of probe molecules such as CO, NO, C\(_2\)H\(_4\), alcohols, ethers and amines, and even N\(_2\) adsorb on the supported Cr(II). Acetylene is converted to benzene and oxygen reoxidizes the catalyst with a bright chemiluminescence, regenerating the surface chromate \[^7-9\].

![Scheme 5.1](image)

**Scheme 5.1**
After reduction of the calcined catalyst with CO three different Cr(II) species are proposed to be present, labeled Cr(II)\(_A\), Cr(II)\(_B\), and Cr(II)\(_C\). They are assumed to be single Cr atoms bound to the silica through two oxygen bridges. Cr(II)\(_A\) features two empty coordination sites capable to bind probe molecules like CO or C\(_2\)H\(_4\). On the other two Cr(II)-species these sites are blocked by one or two oxygen atoms, respectively. High calcination temperatures and low reduction temperatures favor the formation of Cr(II)\(_A\) and yield catalysts with high polymerization activity.
The amount of probe molecules that can be adsorbed per chromium atom is dependent on the preparation. Low calcination temperature and high reduction temperature yields catalysts with lower adsorption capacity, meaning lower coordination unsaturation. At least three different classes of divalent Cr(II) species are thought to exist on silica with two, one or no free coordination site for CO or ethylene chemisorption, labeled Cr$_A$, Cr$_B$ and Cr$_C$ respectively. These species are usually depicted as isolated Cr atoms (figure 5.1), which are bound to the silica surface through two oxygen atoms (Cr$_A$). One or two additional oxygen atoms may be coordinated to the chromium (Cr$_B$ and Cr$_C$ respectively). Surface siloxane (Si-O-Si) or silanol (SiOH) groups are thought to be the sources of these additional oxygen atoms\cite{7,8,10,11}. Their assignment is mainly based on TPD-TPO, IR and UV-vis experiments on silica-gel based catalysts. Note, however, that one group has found IR bands, which they assign to adsorbed CO bridging two Cr atoms\cite{12,13}. This implies that at least some chromium atoms have close neighbors or are even paired, but this does not necessarily mean that the active sites requires paired chromium atoms as the authors suggest. In addition XPS has been used to quantify the amount of two Cr(II)-species (one active one not) and Cr(III). Unfortunately only the result of this analysis is presented and no spectra or fits are presented.

Naturally the twofold coordinatively unsaturated Cr(II)$_A$ is associated with high catalytic activity while especially Cr(II)$_C$ is thought to be far less active. This explanation sounds reasonable and agrees with chemical intuition, certainly the active site needs at least two adsorption sites like in Cr(II)$_A$ to accommodate the growing polymer chain and the incoming ethylene molecule. Furthermore this model gives a convincing explanation, why increasing calcination temperature yields higher activity catalysts. However, increasing the temperature above 350°C during reduction with CO actually decreases the coordination unsaturation of the catalyst\cite{14} and also the catalytic activity for ethylene polymerization even though carbon monoxide is an excellent medium for the dehydroxylation of the silica surface (CO + 2 SiOH $\rightarrow$ CO$_2$ + SiOSi + H$_2$). Furthermore increasing the chromium loading at a given calcination temperature to titrate the surface hydroxyl groups does not increase the activity of the catalyst. On the contrary the activity of the catalyst per chromium atom increases when decreasing the chromium loading of the catalyst\cite{3}.

The last two pieces of evidence are indications that site blocking by hydroxyl groups alone cannot explain the observed trends in the catalytic performance of the Phillips catalyst. The decrease of coordination saturation and the catalytic activity of the supported chromium
during high temperature treatment with CO is probably the result of dimerization or clustering of the Cr(II) species which may become mobile under these severe conditions, a second calcination step restores the catalytic activity \[15\]. Thus not only neighboring surface hydroxyls but also a second chromium atom which facilitates dimerization seem to be detrimental for the catalytic activity.

In addition each of the three Cr(II) species represent a broad class of chromium sites rather than a defined unit. A general feature of most Phillips-type catalyst is the broad molecular weight distribution of the polymer product, which is pointing towards a wide variety of active sites. Each site presents its own catalytic performance depending on the exact coordination environment of the active chromium center, which again depends on the exact preparation of the catalyst. Finally most of the catalysts used in the studies presented here contain also some Cr(III), which is probably present in small Cr$_2$O$_3$-clusters. The role of the surface atoms of these clusters has not been considered. It is assumed to be inactive but Kuhlenbeck et al. \[16\] found that CO weakly chemisorbs on a thin film Cr$_2$O$_3$ single crystal. These single crystals are chromium(II) terminated if the crystal is flashed to 1000K in UHV. Zaki and Knözinger observed a similar behavior on Cr$_2$O$_3$ microcrystallites.

During thermal activation of the Phillips catalyst surface hydroxyls condense to form surface siloxane and at the same time the supported chromium becomes more active for ethylene polymerization. This correlation is used in industry to control the reactivity of the catalyst. However the molecular reason for this correlation is not necessarily straightforward. Apart from removing potential ligands for the active (reduced) chromium the dehydroxylation of the support during calcination also creates stress in the surface or the silica gel, that (possibly) induces a change in the coordination sphere of the chromium resulting in changes in its reactivity. In addition high temperature calcination is also effective to isolate chromium on the silica support as high local chromium coverages are not stable against desorption at high temperatures in dry air (\rightarrow chapter 3). High temperature treatment in CO might reverse this trend probably because the highly unsaturated reduced Cr species form aggregates.

### 5.1.4. Prospects for the CO-reduced CrO$_x$ / SiO$_2$ / Si(100) model catalyst

From the previous section we can conclude that the CO-reduced CrO$_x$ / SiO$_2$ system is an interesting and challenging target for the SiO$_2$ / Si(100) model support. This system is one
step closer towards the active state or the Phillips catalyst as it polymerizes ethylene even at room temperature and below, without “induction period” nor need for a cocatalyst. Even though the reduced CrOₓ / SiO₂ catalyst has been extensively studied using silica gels more or less similar to industrial preparations, the molecular structure of the silica bound chromium is not known.

A systematic XPS and SIMS analysis of the CO-reduced CrOₓ / SiO₂ / Si(100) catalyst varying initial loading, calcination and reduction temperature could reveal the degree of clustering of the supported chromium, starting from well defined calcined catalyst featuring exclusively anchored monochromate. We hope that we will also be able to quantify the hydroxyl population on the supported and unsupported catalyst in dependence of the pretreatment using SIMS (analysing the SiₓOᵧ / SiₓOᵧH ratio) and chemical titration (e.g. with Zn(CH₃)₂[17]. Measuring the interaction of the reduced chromium with probe molecules is probably the most intriguing and ambitious goal we can set for our “realistic surface science model” of the Phillips catalyst. The amount of probe molecules like CO or ethylene which can be chemisorbed per unit area of catalyst, and the strength with which they are held by the supported chromium, is certainly sensitive towards the exact molecular state of the chromium species present, just as their catalytic activity is. Saying this immediately brings us to well established surface science technique called thermal desorption[18] which has widely been used to study the desorption kinetics of adsorbates on single crystal surfaces but has also been applied to model oxide supported metal catalysts[19]. Figure 5.2 gives a schematic impression of the TDS experiment for the few readers who do not know much more about this technique than I do. The TDS spectrum plots the desorption rate of the adsorbate vs. the temperature of the sample. It contains semiquantitative information about the adsorbate coverage and can be analyzed in terms of the Arrhenius law to determine the desorption kinetics of the system (e.g. CO on CrOₓ / SiO₂ / Si(100)). The most simple of these methods proposed by Redhead [20] uses only the maximum of the desorption peak and the heating rate to determine the desorption energy. Combining all this data without prejudices and correlating it to the catalytic activity of the model catalyst should contribute a lot to a molecular level understanding of the Phillips catalyst. This would certainly be an impressive demonstration of the realistic model catalyst approach.

The major obstacle that has prevented us from analyzing the CO reduced CrOₓ / SiO₂ / Si(100) catalyst is related to the extremely high reactivity of the coordinatively unsaturated
Cr species together with the extremely small amount of surface chromium that we are working with. We have already experienced how delicate our model catalyst can become when we reduced it with ethylene during the transition period of the polymerization experiments (→ chapter 4). The only environment that can assure a reasonable lifetime of the reduced catalyst is ultra high vacuum or extremely clean preparation conditions, e.g. the CO at atmospheric pressure and above 350°C. The critical step is the transient between the reaction conditions that form the reduced chromium catalyst and the transfer to the analysis chamber. In our current experimental setup the preparation chamber (→ chapter 2) this transfer goes wrong, as the residual gas (base pressure $2 \times 10^{-6}$ mbar) is not sufficiently oxygen free. This chamber is simply not build for these kind of experiments but to facilitate fast entry of technical samples into the UHV. Thus if we intend to characterize the CO-reduced CrO$_x$ / SiO$_2$ / Si(100) catalyst we have to come up with a better preparation chamber that is compatible with our VG-chambers. It should be a true UHV chamber with a base pressure below $10^{-9}$ mbar, equipped with a reactor for atmospheric pressure and preferably a built-in TDS setup. Technical speaking in my opinion this preparation/TDS chamber can be realized, though I expect that it would be quite an effort. If it will ever get a real chance is simply a matter of priorities. Being somewhat emotionally involved with the realistic side of model catalysis I shall say no more.

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**Figure 5.2**

*In a TDS experiment the sample is exposed to an adsorbing gas at low temperature. Subsequently the vacuum system is evacuated and the sample is heated usually with a linear heating rate. The desorbing gasses are monitored with a mass spectrometer. The TDS spectrum plots the desorption rate of the adsorbate vs the temperature. It contains information about the adsorbate coverage as well as the desorption energy.*
5.2. Ethylene polymerization and the flat CrO$_x$/SiO$_2$/Si(100) model catalyst

The flat CrO$_x$/SiO$_2$/Si(100) model catalyst produces polyethylene at 160°C and 1 atm C$_2$H$_4$ with a constant and reasonably high activity. This activity can be measured conveniently with atomic force microscopy, analyzing scalpel scratches of the polyethylene film that develops on the flat substrate. We can observe the development of the crystalline architecture of the polyethylene film after crystallization of the polymer. In the micrometer to sub-micrometer range we have followed the development of polyethylene spherulites (figure 4.7, 4.8), the well-known superstructure of melt crystallized polyethylene lamella crystals. The thickness of the polymer can be controlled either through varying the polymerization time or the catalyst loading. At a film thickness below 40 nm we observe a closed layer of stacked lamella crystals growing in perfect edge-on orientation with respect to the surface. We can image nm details in these lamella crystals and we find a grainy substructure in the lamella core. A similar morphology has been described recently by Strobl et al. [21] for syndiotactic polypropylene and suggests that polyolefins in general develop lamella crystal from preformed structures that represent building blocks of less perfect “native crystallites”. These crystallites may subsequently anneal to create the final (more or less perfect) lamella crystal. Our measurements are at least supporting evidence for these ideas that are in contradiction to the classical view of polymer crystal growth, which describes the lamella growth to proceed segment by segment [22,23]. This is nice spin-off of our work and it demonstrates the potential of the combination flat model catalyst and AFM.

However, the unique characteristic of this model catalyst with respect catalytic olefin polymerization is that the polymer is actually produced on the flat surface by active sites, which are anchored to support. We have exploited this feature the CrO$_x$/SiO$_2$/Si(100) system following two ideas. The first one is decreasing the active site concentration until each isolated site produces an isolated polymer island on the flat support. Preliminary experiments described in section 4.5 indicate that this is indeed possible and that we can even estimate the catalytic yield can of each individual active site. We hope that our current systematic study of the catalyst with extremely low loadings (around 100 Cr/µm) will give us a quantitative picture of the catalytic activity of this system literally on a molecular level.

The other main theme of the “flat olefin polymerization catalyst approach” that we have explored in the scope of this thesis deals with what is called the nascent morphology of
polyolefins. Nascent morphology of polyolefins is the result of the catalytic polymer formation below the melting temperature. In the next few section we will give a short introduction to the subject and present our preliminary results obtained on the CrOₓ/SiO₂/Si(100) system. The AFM images shown in here are to the best of our knowledge the first visualization of such morphology at nm resolution, as normal reactor powders are simply not suited for high resolution microscopies.

5.3. Nascent morphology of polyolefins and the flat CrOₓ/SiO₂/Si(100) model catalyst

5.3.1. Introduction

In chapter 4 we discussed polyethylene films, produced at 160°C, which means that the polymer is initially present in the molten state. After reaction the polymer was cooled to 100°C for at least 1 hour to allow crystallization. The AFM images of the surface morphology were taken at room temperature and they show the development of polyethylene crystallization under confined conditions (defined film thickness). If the catalytic polymerization of ethylene takes place below the melting temperature of polyethylene (about 133°C) the formation of the polymer chain and the self-organization of the chains to larger entities (crystallization) take place simultaneously. As a consequence such polymer has a different crystal architecture than the same polymer that has been crystallized from the melt, resulting in different physical properties. For example nascent polyolefins usually show a higher melting temperature and higher crystallinity than the same material that has been in the melt once.

The nascent morphology of polyolefins has been a rather neglected topic in polymer physics partly because the reactor powder of industrial polyolefins first is molten in an extruder and has lost all information of its catalytic origin before it leaves the plant. These plastics are usually processed and formed by injection molding. Hence nascent morphology simply is not an issue for these polymers except for the polymer particle shape on the µm to mm scale and the fracturing of the catalyst particle during polymerization [24].

However, a number of high performance polymers with very high molecular weight, e.g. UHMW-PE cannot be processed with injection molding, due to their high viscosity in the melt. Even though they offer very attractive mechanical properties, they fall short of their full potential because they are processed by sintering techniques. As a result of the limited
diffusion of the polymer chains even the final product retains some of the nascent morphology of the polymer in the form of grain boundaries, which limit the mechanical strength of the product.

In other words the nascent morphology of the reactor powder (its crystallinity, crystal size and the diffusivity of the polymer chains) can have a direct influence on the processibility and the quality of a polymer product.

The unusual high melting temperature of many nascent polyolefins is attributed to the formation of extended chain crystals during polymerization \[25\], more or less similar to the formation of cellulose fibrils in nature. Other authors claim that the high melting temperature is related the formation of highly metastable folded chain polymer crystals during polymerization, which reorganize prior to melting \[26,27\].

The study of nascent polymer morphology on a nanometer or even atomic (orientation of the polymer chains) level is hampered by the fact that the (supported) catalyst usually fragments during polymerization and produces a material that is ill suited for high resolution microscopies like AFM, STM or TEM. We feel that planar supports for olefin polymerization catalyst offer a key to monitor and control polymer growth on catalyst surfaces and our initial results using the CrO\textsubscript{x} / SiO\textsubscript{2} / Si(100) system are reported in the following section.

5.3.2. Low temperature ethylene polymerization using flat CrO\textsubscript{x} / SiO\textsubscript{2} / Si(100) model catalyst - first images of nascent polyethylene

The simplest way to produce nascent polyethylene with the CrO\textsubscript{x} / SiO\textsubscript{2} / Si(100) model catalyst is to use a calcined catalyst and treat this catalyst with ethylene at 1 atm below 133°C. If a lower polymerization temperature is used we have to take into account that the reduction of the anchored chromate by ethylene is slowed down, which becomes evident as the so called induction period. The time that ethylene needs to activate the catalyst increases with decreasing polymerization temperature until at 60°C no polymerization takes place.
Figure 5.3
Surface morphology of nascent polyethylene (left) and of polyethylene as crystallized from the melt (right). Height contrast for both images is 20 nm, description see text.
We chose a calcination temperature of 650°C and a polymerization temperature of 115°C in order to minimize the induction period. Figure 5.3 shows an AFM image (height (contrast 20 nm), amplitude and phase contrast) of a polyethylene film produced at 115°C (left) in a 60 min polymerization run (including induction period which we cannot measure). The polymer film has a thickness of about 20 - 30 nm. A polyethylene film of similar thickness but crystallized from the melt is also shown for comparison (right). While the melt

![AFM image of polyethylene film](image1)

**Figure 5.4**
Polyethylene “worms” produced on the CrO$_x$ / SiO$_2$ / Si(100) catalyst at 115°C show a uniform width of about 45 nm and extend up to several hundred nm in length. The height contrast in this 1*1 µm$^2$ zoom of figure 5.3 is 20 nm. The nature of the polyethylene worms is unknown. They seem to grow completely independent from each other. In some regions they appear to even grow on top of each other (white circle). On the other hand in phase contrast they appear as folded chain fibrils (white arrow) with a crystalline, hard core (bright contrast) sandwiched between two amorphous, soft regions (dark contrast).
crystallized polyethylene film shows staked, edge-on lamella crystals as discussed in section 4.4.2. The nascent polymer features a worm-like structure. The worms have a uniform width of 45-50 nm and show no long range ordering. There are even indications in figure 5.4 that they can grow ontop of each other.

On the other hand when we look at the phase contrast, we see we see that our “worms” actually show a hard (crystalline) core, sandwiched between soft layers. In this respect they appear as perfect folded chain crystals in edge-on orientation with a homogeneous (no grainy submorphology) crystalline core that extends over micrometers in length. If we compare the height images the nascent and the melt crystallized sample we see that latter is quite homogeneous in height. The nascent polyethylene sample shows that the highest polymer worms are embedded in a thinner polymer layer only 0-5 nm in height. If two worms touch each other there seems to be a tendency for parallel alignment.

Even if we assume that the polyethylene “worms” are indeed lamella fibrils in-edge on orientation toward the silica surface, they probably have formed in a very different fashion than melt crystallized polyethylene. One possible scheme is that the nascent crystals grow by subsequent incorporation of individual polymer chains, which are continuously produced at the active sites. This makes the formation of entanglements between polymer chains or of tie molecules between neighboring folded chain crystals very unlikely. Consequently the polymer chains would exhibit a higher mobility in the solid polymer, which could explain the unusual high first melting temperature of many nascent polymers \[26,27\]. We want to stress however that our experiments so far are only on a proof of principle level and that there are indications that the nascent morphology of polyethylene is a quite complex story. In fact in the same experiment we observed a very different morphology than the “worms” we have described so far. This morphology depicted in figure 5.5 looks somewhat like fish scales. It consists of plate-like structures, which are aligned in almost perfect order. These plates overlap each other as in a fir-cone. We even observe a combination of the fir cone and the “worm-like” morphology on the same image. The most straightforward speculation that offers some explanation for this surprising observation is that the fish scales are actually lamella crystals that for some reason are no longer in edge-on orientation but grow almost parallel to the surface. As they are no longer sterically constrained they grow in both a and b direction. Quite intriguingly they look just as lamella single crystals do. Again we stress that we are dealing only with one set or samples all being polymerized in one experiment. It is certainly allowed to base some more
Conclusions and Outlook

or less hand-waving speculations on this but to put these speculations on more solid foundations we need many more experiments. A first step should be a systematic view on the evolution of nascent polyethylene depending on polymerization temperature, film thickness and possibly active site concentration. Unfortunately the calcined CrO₅ / SiO₂ / Si(100) system shows a drastic decrease in polymerization activity when decreasing the polymerization activity towards the 100°C range and we expect no activity at temperatures below 60°C. Attempts to polymerize over CO-reduced catalyst (section 5.1.3) have not been successful jet, either because we did not succeed in completely removing the CO before polymerization, which renders our catalyst poisoned, or more likely because the catalyst reoxidized during the cool down of the reactor.

![Figure 5.5](image)

**Figure 5.5**
At least two different “nascent morphologies” of polyethylene have been observed on the same set of CrO₅ / SiO₂ / Si(100) wafers. A pure worm-like structure (top-left) as discussed earlier, a pure scale-like structure (bottom-right) and even a combination of both (middle).
5.4. *Broadening the scope – catalysis meets polymer physics*

Apart from low density polyethylene that is produced by a high-pressure radical process, almost all polyolefins are produced catalytically at intermediate pressures between 1 and 50 bar and low temperatures typically between room temperature and 180°C. Polyolefins include polyethylene, polypropylene and copolymers of ethylene and a second alkene, typically an α-olefin to produce linear low density polyethylene. Catalytic systems are usually rated in terms of activity (amount of polymer per amount of catalyst) and selectivity of the catalytic reaction. The selectivity of the catalytic reaction controls the molecular properties of the polymer chain. The relative rate of chain growth versus the chain termination reaction determines the average molecular weight, the stereoselectivity of monomer insertion controls the tacticity of the polymer as in isotactic polypropylene. In the case of copolymerization the relative rate of incorporation of the comonomer (α-olefin) with respect to ethylene determines the amount of alkylbranching in linear low-density polyethylene (chemoselectivity). The reactivity of the active site is controlled by varying the coordination sphere of the active metal center. This can be done on the molecular level using metallocene catalysts of the early transition metals, which yield well-characterized single site catalysts producing well defined polyolefins in a homogeneous solution. On a large scale industrial production the gas-phase mode using a heterogeneous catalyst is preferred, partly because this gives a better control over the shape of the produced polymer particles and of course they avoid a costly removal of the solvents. Consequently, the heterogenization of homogeneous olefin polymerization catalysts has become a field of research in its own right.

Most polymers reach their application not in the nascent form but after being processed in the melt (e.g. in an extruder). In this form they are also the subject of polymer physics, which seeks correlations among e.g. structure of the chains, thermodynamics, viscoelastic behavior, crystallization and finally the performance of the material during processing and end use. The melting of the nascent reactor powder in a way separates the catalytic from the physical side of these polyolefins as all structural peculiarities of the nascent morphology are lost. The only way catalysis can influence the properties or performance of these polymers is by controlling the assembly of the polymer chains. However, this is not true for all polyolefins:
Figure 5.6
Schematic view of the relevant processes concerning olefin polymerization: the formation of the catalyst and the active site occur in the Å to nm range as does the formation of the polymer backbone. The self organization of the polymer chains to form the (nascent) morphology appear in the nm to µm regime, making the combination of flat model catalysts and AFM an ideal tool for their exploration. Industrial polymerization catalysts fracture during polymerization. The catalyst particle of about 100 µm in diameter grows to polymer particles of several mm, while maintaining its shape.
Some polyolefins, e.g. ultra-high molecular weight polyethylene (UHMWPE, \( M_w > 3 \times 10^6 \text{ amu} \)) that features an extremely high viscosity in the melt, cannot be processed in the melt by injection molding or similar techniques. It is processed by sintering the nascent reactor powder. UHMWPE is a potentially very attractive high performance plastic used e.g. in knee joints due to its superior wear-resistance. However, the restricted diffusion of the polymer chains during sintering limits the mechanical strength of the product as the sintered polymer particles develop grain boundaries instead of one homogeneous phase. In this example it can be envisaged that improving the exchange of polymer chains between the polymer particles (grains) might improve the performance of the polymer. One straightforward approach would be to decrease the crystallite size or to transform the UHMWPE to the hexagonal phase, which has a high inherent chain mobility [28].

The previous example illustrates that the nascent morphology of polyolefins can have direct impact on the processability and the performance of polymer in its final application. As we have pointed out earlier we feel that the flat model catalyst produces ideal polymer films for morphologic studies with AFM at nm resolution. We want to use this approach to systematically map the nascent polyolefin morphology and at the same time control the catalytic system, especially the heterogenization of the active phase. Figure 5.6 gives an impression of the length scale of the relevant processes during olefin polymerization. As the nascent morphology is the result of simultaneous chain growth and crystallization we expect to find several metastable modifications of nascent polymer depending on the exact mode of polymerization. While it is totally unclear how the polymer chains arrange themselves to form crystallites, it is reasonable to assume that rate of production of the polymer chains on the catalyst and the chain mobility during polymerization determine the morphology that the growing polymer will develop.

### 5.4.1. Alternative Catalysts

Regarding the nascent morphology of polyolefins the calcined \( \text{CrO}_x / \text{SiO}_2 / \text{Si}(100) \) model catalyst that we have developed in thesis has some major limitations, as the catalytic yield decreases drastically with decreasing temperature and only polyethylene (maybe some copolymers) can be produced. As we already pointed out in section 5.1.3 the Phillips catalyst can be activated for low temperature ethylene polymerization with reducing agents like CO or metal alkyls. Unfortunately we have not succeeded in doing so with our \( \text{CrO}_x / \)
SiO$_2$ / Si(100) model catalyst – we will keep on trying though. Parallel to this work with the Phillips system we plan to adapt our flat model catalyst approach to other polymerization catalysts. Exploratory experiments using a Cr(Cp)$_2$ / SiO$_2$ / Si(100) system prepared by evaporation [29] and a CpZrCl$_2$ + MAO / SiO$_2$ / Si(100) by spincoating impregnation have already been done. Our initial objective in our attempts to use organometallic catalysts is quite pragmatic: they are very versatile and can produce a wide variety of polyolefins including stereoregular polypropylene and UHMWPE at low temperature with high activity.

However, these catalysts are experimentally at least as challenging as the CrO$_x$ / SiO$_2$ / Si(100) system because they exhibit, again, an extremely small amount of very reactive species. At least in the case of the CpZrCl$_2$ + MAO / SiO$_2$ / Si(100) catalyst we have some indications that it has produced polyethylene. This catalyst has been prepared by spincoating impregnation in a glovebox and was treated with ethylene at atmospheric pressure and 60°C. Figure 5.7 shows a series of XPS spectra of these catalysts. The active catalyst (“Zr+MAO”) features the strongest C1s peak. Atomic force microscopy (figure

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Figure 5.7
A mixture of ZrCp$_2$Cl$_2$ + MAO (1:10) that has been spincoating onto the SiO$_2$ / Si(100) support shows a large C 1s peak after treatment with 1 bar ethylene at 60°C for 1h, while MAO alone shows no significant C 1s signal. This implies that the “Zirconocene model catalyst” has produced a small amount of polyethylene.
5.8) is less revealing as on the CrO₃ / SiO₂ / Si(100) catalyst, mainly because the large amount of co-catalyst (MAO) dominates the surface morphology. Upon contact with air MAO (methyl aluminium oxide) converts quantitatively to Al₂O₃ that can be removed with dilute acid. These preliminary results may not look impressive on first site but based on our 4 years experience with the CrO₃ / SiO₂ / Si(100) catalyst they are quite encouraging. This is only the beginning.

![Figure 5.8](image)

*Figure 5.8*
Surface morphology of methyl-aluminium oxide (MAO, left) and of ZrCp₂Cl₂ + MAO (right) spincoated onto the SiO₂ / Si(100) model support. The images are recorded with AFM in amplitude contrast. Both samples have been treated in 1 bar ethylene at 60°C for 1 hour. The spherical particles are most likely small Al₂O₃ particles formed upon exposure of the MAO surface to air after the polymerization experiment. The alumina particles are much smaller on the zirconocene model catalyst (right), presumably because the MAO has been embedded in a polyethylene matrix.
Reference List

Summary

The Phillips ethylene polymerization catalyst currently accounts for slightly less than one third of the world’s production of linear high-density polyethylene. The original catalyst has been patented in the late fifties. Nowadays a whole family of Phillips catalysts exists optimized to produce a variety of polyethylene grades. This industrial catalyst development is based on rather empirical research, however, because the catalyst has proven to be quite difficult for most spectroscopies partly due to the low chromium loading (less than 1 wt% ≈ 0.4 Cr/nm$^2$) of the industrial catalyst. In addition the active surface is hidden inside the sponge-like, non-conducting silica support which makes the application of surface spectroscopies difficult. Consequently the molecular level picture of the Phillips is still quite vague (⇒ 3.1; 5.1.3).

One way to obtain a more detailed information about the catalytically active surface is via model catalysts, which are designed to boost the performance of spectroscopic techniques employed. Surface science techniques work best on conducting, flat substrates, thus surface science model catalysts are often based on thin oxidic films grown on a metal substrate. Emphasizing resemblance with “real life” heterogeneous catalysts, our group strives to imitate the industrial catalyst preparation as closely as possible. These “realistic” surface science models maintain the same surface chemistry as their industrial counterparts.

We have explored the Phillips system to demonstrate the potential of this model catalyst approach. Our model catalyst imitates the simplest member of the Phillips catalyst family (the original Phillips catalyst) prepared by pore-volume impregnation of aqueous chromic-acid ($\text{CrO}_3$) on silica. The flat model catalyst is prepared on a calcined silicon wafer that features a thin layer on the surface silica. The chromium is deposited onto the fully hydrolyzed silica surface by spincoating impregnation from aqueous chromic acid. This technique, which resembles the pore-volume impregnation of silica gels, gives full control over the catalyst loading, which has been varied between 0 and 10 Cr/nm$^2$.

This thesis covers the preparation, UHV characterization and catalytic testing of the CrO$_x$ / SiO$_2$ / Si(100) model of the Phillips ethylene polymerization catalyst. Section 2 deals with the experimental details of the employed surface probes as well as the experimental tools (reactors) that we developed to handle this somewhat delicate model catalyst.
In section 3 we describe the thermal activation of the model catalyst. The impregnated catalyst is calcined in dry artificial air at temperatures between 400° and 730°C. We follow the molecular state of the supported chromium with a combination of X-ray photoelectron spectroscopy (XPS), secondary-ion mass spectrometry (SIMS) and Rutherford backscattering spectrometry (RBS). In agreement with general consensus we observe the initially hydrated chromate anchoring to the silica support in an esterification reaction with the surface silanol groups. The amount of chromate that can be anchored in such a fashion is naturally limited by the amount of surface-hydroxyl (silanol) groups present and decreases with increasing calcination temperature.

There is still a great deal of uncertainty regarding the molecular structure of the anchored chromium in the literature (→ section 3.1). Different authors propose monochromate, dichromate and even polychromate to be among the anchored species, while the superficial chromium is transformed to inactive chromium(III) oxide. Our study reveals the structure of the silica bound chromium species being exclusively monochromate, independent of initial chromium loading or calcination temperature.

At high chromium loadings and high calcination temperatures the superficial chromium desorbs from the silica, which works as a mechanism to isolate the active species. Because of the desorption the maximum amount of chromate that can be anchored to the silica support decreases with increasing calcination temperature. No Cr$_2$O$_3$ is formed on the flat silica substrate, however, the desorbing chromate readily readsorbs on an empty silica surface. We propose that chromate-adsorption and -readsoption also happen inside the pores of silica gels acting as a mechanism to redisperse the impregnated chromium. Excess chromium trapped inside the pores of a silica gel eventually forms Cr$_2$O$_3$-clusters. What is presented as spectrosopic evidence for the presence of dichromate or even polychromates on calcined CrO$_x$/SiO$_2$ catalysts may actually be due to formation of surface chromates on Cr$_2$O$_3$-clusters.

In section 4 we address ethylene polymerization over the CrO$_x$/SiO$_2$/Si(100) catalyst. The model system features a reasonable catalytic activity at 160°C, comparable to that of the industrial catalyst. The catalytic activity increases with increasing calcination temperature. The polymer that develops on the CrO$_x$/SiO$_2$/Si(100) catalyst initially forms a closed, molten film (melting temperature ≈ 133°C), which crystallizes upon cooling to 100°C.
The film thickness can be controlled through varying either polymerization time or catalyst loading. The polymer films are well suited for atomic force microscopy. We observe the expected morphology for melt crystallized polyethylene, however, at nanometer resolution we notice, for the first time for polyethylene, a substructure in the lamellar crystal architecture. Decreasing the chromium loading corresponds to increasing the average distance between the active sites. If the catalyst loading becomes sufficiently small, we observe small, isolated polymer islands, which we believe, are the product of solitary active sites, i.e individual chromium atoms. The catalytic activity of each active site can be estimated using height-contrast AFM images.

In section 5 we try to point out some possible future developments of the flat model catalyst approach that either directly concern the CrO$_x$ / SiO$_2$ / Si(100) system or at least have been inspired by it.

The calcined CrO$_x$ / SiO$_2$ / Si(100) model catalyst is reasonable well characterized, however, we found no explanation why increasing the calcination temperature yields a catalyst with higher polymerization activity. In literature the increase in catalytic activity upon increasing calcination temperature is attributed to a decrease in surface hydroxyl population on the silica support. Surface hydroxyls are believed to block adsorption sites on the chromium center. Evidence for this view is deduced from CO-reduced catalysts that adsorb probe molecules (e.g. CO). The CrO$_x$ / SiO$_2$ / Si(100) model catalyst could provide a very detailed picture of the CO-reduced catalyst if we combine structural information of the supported chromium (XPS, SIMS) with a quantification of the surface hydroxyl groups (chemical titration, XPS, SIMS) and finally a description of the adsorption behavior of the supported chromium (TDS).

Finally we turn our attention towards the morphology of the polymer film that is produced on the flat model catalyst below the melting temperature of the polymer (133°C). Under these conditions the formation of the polymer chains and the self-organization of these chains (crystallization) happen simultaneously. Nascent polymer shows different physical properties (e.g. melting temperature) than the same material that has been in the melt once.

The flat model catalyst approach using the CrO$_x$ / SiO$_2$ / Si(100) system or any other olefin polymerization catalyst offers a unique opportunity to explore nascent polyolefin morphology on a nanometer detail using AFM. The first successful attempt to image
nascent polyethylene produced with a calcined CrO\textsubscript{3} / SiO\textsubscript{2} / Si(100) catalyst at 115°C is presented.
Samenvatting

De Phillips ethyleen polymerisatiekatalysator wordt tegenwoordig gebruikt voor ongeveer dertig procent van de wereldproduktie van lineaire hoge-dichtheidpolyethyleen. De oorspronkelijke katalysator werd gepatenteerd achter in de vijftiger jaren. Tegenwoordig bestaat er een hele reeks van het type Phillips katalysator voor de produktie van verschillende kwaliteiten polyethyleen. De ontwikkeling van deze industriële katalysator is gebaseerd op onderzoek van empirische aard, aangezien deze tamelijk moeilijk te onderzoeken is met spectroscopische technieken vanwege de lage hoeveelheid chroom (minder dan 1 gew% ≈ 0.4 Cr/nm²) in de katalysator en het feit dat het aktieve oppervlak aan het oog van de meetapparatuur wordt onttrokken door het sponsachtige, niet geleidende silicabedragermateriaal. Hierdoor is op het moleculaire niveau nog weinig bekend over de Phillips katalysator (→ 3.1; 5.1.3).

Een manier om meer gedetailleerde informatie over het katalytisch aktieve oppervlak te verkrijgen is via een modelkatalysator, welke ontworpen is om spectroscopische methoden beter te kunnen toepassen. Oppervlakte technieken werken het best op geleidende, vlakke dragmaetalen en daarom zijn modelkatalysatoren vaak gebaseerd op dunne oxydische lagen die op een metalloppervlak gegroeid zijn. Door nadruk te leggen op ‘werkelijke’ heterogene katalysatoren streeft onze groep het zo goed mogelijk imiteren van de industriële katalysatorbereiding na. Deze ‘realistische’ oppervlakte modellen vertonen dezelfde chemische oppervlakte eigenschappen als hun industriële tegenhangers.

We hebben het Phillips systeem onderzocht om de kracht van deze modelkatalysator benadering te demonstreren. Onze modelkatalysator is een imitatie van het simpelste lid van de Phillips katalysator familie (nl. de originele) die werd bereid door porie-volume impregnatie van waterig chroomzuur (CrO₃) op silica. De vlakke dragmaetal is gemaakt met een gecalcineerde siliciumschijf met een dun laagje oxyde op het oppervlak. Het chroom werd op het oppervlak gedeponeerd op het volledig gehydrolyseerde silica oppervlak door spincoating-impregnatie uit waterig chroomzuur. Deze techniek, welke het porie-volume impregnatie proces van silica gels imiteert, geeft volledige controle over de katalysatorbelading. Deze hebben wij gevarieerd tussen 0 en 10 Cr/nm².

Dit proefschrift beschrijft de preparatie, UHV karakterisatie en het katalytische testen van de CrO₃/SiO₂/Si(100) Phillips modelkatalysator. Hoofdstuk 2 behandelt de experimentele
details van de ge bruikte oppervlaktegevoelige apparaten en het experimenteel gereedschap (reactoren) dat we ontwikkeld hebben om deze ietwat gevoelige modellkatalysator te onderzoeken.

In hoofdstuk 3 beschrijven we de thermische activatie van de modellkatalysator. De geimpregneerde katalysator is gecalcineerd in droge technische lucht bij temperaturen tussen 400° en 730°C. We hebben de moleculaire toestand van het chroom bestudeerd met een combinatie van Röntgen foto-electron spectroscopie (XPS), secondaire ionen massaspectrometrie (SIMS) en Rutherford backscattering spectrometrie (RBS). In overeenkomst met de algemene consensus vinden we dat het initieel gehydrateerde chromaat bevestigd wordt aan de silicadrager door een veresteringsreaktie met de oppervlaketesilanol groepen. De hoeveelheid chromaat die op deze wijze bevestigd kan worden is gelimiteerd door de hoeveelheid hydroxylgroepen aan het oppervlakte, welke kleiner wordt met hogere calcinatie temperatuur. Er is nog steeds grote onzekerheid in de literatuur over de structuur van het bevestigde chroom (→ hoofdstuk 3.1). Verschillende auteurs stellen voor dat monochromaat, dichromaat en zelfs polychromaten bevestigd kunnen worden aan het oppervlak, terwijl het overmatige chroom getransformeerd wordt tot inaktief chroom(III)oxide.

Ons onderzoek toont aan dat de structuur van het aan silika gebonden chroom alleen monochromaat is, onafhankelijk van de oorspronkelijke chroombelading of de calcinatie temperatuur. Bij hoge chroombelading en bij hoge calcinatietemperatuur desorbeert het overtollig chroom van het silica waardoor het aktieve chroom geisoleerd wordt. Wegens deze desorptie vermindert de maximale hoeveelheid chroom dat aan het oppervlak bevestigd kan worden. Cr₂O₃ wordt niet gevormd op het vlakke silica oppervlak, echter het desorberende chromaat kan gemakkelijk reabsorberen op een leeg silica oppervlak. We stellen voor dat chromaat-adsorptie en –readsorptie ook optreedt binnen de porien van een silica gel als een proces voor de redispersie van geimpregneerd chroom. Overmatig chroom dat niet uit de porien kan treden zal Cr₂O₃-clusters vormen. Spectroscoïpische aanwijzingen dat dichromaat of zelfs polychromaten op gecalcineerde Cr₂O₃/SiO₂ katalysatoren aanwezig is kan eventueel het gevolg zijn van de vorming van oppervlakte chromaten op Cr₂O₃-clusters.

In hoofdstuk 4 beschrijven we de ethyleen polymerisatie op het CrOₓ/SiO₂/Si(100) katalysatorsysteem. Het modelsysteem vertoont een redelijke katalytische activiteit bij
160°C, wat vergelijkbaar is met de prestaties van de industriële katalysator. De katalytische activiteit neemt toe bij hogere calcinatietemperatuur. Het polymeren dat ontstaat op het CrO\textsubscript{x}/SiO\textsubscript{2}/Si(100) katalysatorsysteem vormt een gesloten en gesmolten film (smeltemperatuur ≈ 133°C) die kristalliseert tijdens het afkoelen tot 100 °C.

De filmdikte kan worden gevarieerd door ofwel de polymerisatietijd of de katalysatorbelading te veranderen. De polymerfilms zijn goed te bestuderen met AFM. We vinden de verwachte morfologie voor uit smelt gekristalliseerd polyethyleen, echter op nanometer schaal vinden we, hetgeen voor polyethyleen een premiere, een secundaire structuur in de lamellen kristal architektuur. Het verlagen van de chroombelading resulteert in de verhoging van de gemiddelde afstand tussen de aktieve plaatsen. Indien de katalysatorbelading laag genoeg wordt vinden we kleine geïsoleerde polymeriestukjes, oftewel individuele chroomatomen. De katalytische activiteit van elke actieve plaats kan worden geschat aan de hand van hoogte-contrast AFM plaatjes.

In hoofdstuk 5 proberen we eventuele mogelijke ontwikkelingen van de vlakke modelkatalysator-benadering te identificeren welke direct betrekking hebben op het CrO\textsubscript{x}/SiO\textsubscript{2}/Si(100) katalysatorsysteem of in ieder geval geïnspireerd zijn door dit systeem.

Het CrO\textsubscript{x}/SiO\textsubscript{2}/Si(100) katalysatorsysteem is redelijk goed gekarakteriseerd, we hebben echter geen verklaring gevonden waarom het verhogen van de calcinatietemperatuur een katalysator oplevert met een hogere katalytische activiteit. In de literatuur wordt de verhoging van de katalytische activiteit bij verhoging van de calcinatietemperatuur toegeschreven aan een verlaging van de oppervlakte hydroxyl populatie op de silica drager. Oppervlaktehydroxylen zouden adsorptieplaatsen op het chroom blokkeren. Bewijs voor deze uitleg wordt gehaald uit experimenten met CO-gereduceerde katalysatorenpartikelen (bijvoorbeeld CO) adsorberen. Het CrO\textsubscript{x}/SiO\textsubscript{2}/Si(100) katalysatorsysteem zou een zeer gedetailleerde plaatje van de CO-gereduceerde katalysator kunnen geven indien we structurele informatie van het gedragen chroom (XPS, SIMS) zouden combineren met een quantificatie van de oppervlaktehydroxylgroepen (chemische titratie, XPS, SIMS) en met een beschrijving van het adsorptiedrag van het gedragen chroom (TDS).

Als laatste onderzoeken we de morfologie van de polymerfilm die geproduceerd wordt op de vlakke modelkatalysator onder de smeltemperatuur van het polymer (133°C). Bij deze omstandigheden vormen de polymerketens terwijl zij zichzelf inpassen in het systeem.
“Nascent” polymeer vertoont andere fysische eigenschappen (bijvoorbeeld smelttemperatuur) dan hetzelfde materiaal dat ooit gesmolten is geweest.

De vlakke model katalysatorbenadering met gebruikmaking van het CrOₓ/SiO₂/Si(100) katalysatorsysteem of enig andere olefine polymerisatiekatalysator geeft ons een unieke kans “nascent” morfologie van polyolefine op nanometerschaal te bestuderen met AFM. De eerste succesvolle poging om nascent polyethyleen te tonen gemaakt met een gecalcineerd CrOₓ/SiO₂/Si(100) katalysatorsysteem bij 115°C wordt hier beschreven.
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Planar Model Systems for Olefin Polymerization: The Phillips CrO<sub>x</sub>/SiO<sub>2</sub>
Catalyst
*Top.Catal.*, accepted

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The State of the Supported Chromium during Thermal Activation of the CrO<sub>x</sub>
/ SiO<sub>2</sub> (Phillips) Ethylene Polymerization Catalyst,
in preparation
Acknowledgement

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Curriculum vitae

Peter Thüne was born on May 25th 1967 in Buxtehude, Germany. He finished grammar school (Halepaghen Gymnasium Buxtehude) in 1987. In the same year he started his chemistry study at the Rheinische Friedrich Wilhelms Universität, Bonn. He passed the graduation exams in November 1994. In the surface science group of Prof. Dr. K. Wandelt he worked in his graduation thesis on the “Electrochemical Oxidation of Carbon Monoxide over Tin-Platina Model-Electrodes” at the Institut für Physicalische und Theoretische Chemie der Universität Bonn. He achieved his University Diploma in Chemistry in November 1995.

On December 1st 1995 he started his Ph.D. thesis under supervision of Prof. Dr. J.W. Niemantsverdriet at the Laboratory of Inorganic Chemistry and Catalysis of the Eindhoven University of Technology, which is part of the Schuit Institute of Catalysis. The most important results of this work are described in this thesis.