Transmission electron microscopy on live catalysts

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CHAPTER 1

Introduction

1.1   Why is catalysis important?

Catalysis pervades our daily lives in countless ways. Some applications of catalysts are well-known, for example the three-way catalytic converters that are mounted on the exhausts of our cars. By using these, we try to make the impact of our cars on the environment less severe. Harmful and toxic gases are removed, as the catalyst converts these into less dangerous products.[1] Also, the fuel that we put into our cars is processed and cleaned thoroughly by a series of catalytic treatments, as it originates mostly from crude oil, which is contaminated (e.g. with sulfur, as we will see below). Not only the automotive industry exploits catalysts: the pharmaceutical industry, chemical plants, food processing industries, the production of polymers, they all rely on catalysts to make their production process easier, more energy efficient, and overall cleaner.[2,3]

Why are catalysts so special, why are they popular in all these processes and why are so many industries dependent on them? The reason for this is rooted in the working principle behind catalysis in general. A catalyst can enable or improve a chemical reaction between two (or more) reactants. Various aspects of a chemical reaction can be improved by adding a catalyst, for example the reaction rate, the selectivity, and the energy required to let the reaction take place.

In heterogeneous catalysis for example, when two reactants react with each other to form a product, a type of catalyst that is frequently used consists of metal nanoparticles, supported on a high surface-area metal oxide material. The surface of the metal nanoparticles facilitates the adsorption of the reactant molecules, allows them to react, and subsequently releases the newly formed molecules. The reactant molecules can be in gas or in liquid phase, while gaseous reactants could also form liquid phase products, for example in the Fischer-Tropsch process, which is the formation of liquid hydrocarbons from CO and H_2 gas. Different types of metals have different properties, so a chemical reaction that will take place on the surface of a nickel nanoparticle, might not necessarily give the same result on e.g. a platinum nanoparticle. Also, the catalytic properties of a metal nanoparticle can be altered by mixing multiple metallic elements into an alloy, by changing the support material carrying the nanoparticles, or by varying the size or shape of the nanoparticles.[4-9]

The performance of a catalytic system can therefore be tuned by actively changing the parameters mentioned above. These adjustments might result in a catalyst that is more active, has a longer lifetime before becoming inactive, or requires less energy to yield the same result (e.g. to require a lower operating temperature or pressure of the reactants). Also, the selectivity of the chemical reaction can be tuned, so that more of the desired end products are formed, while side product formation is suppressed.

As catalysts are used so abundantly, even the smallest improvements can lead to significant savings in energy, materials, or other costs. For this reason there is an ongoing effort in academia and industry to try and improve the catalysts used in their processes.

1.2   Research in catalysis, then and now

The search for better catalysts has evolved significantly since the early days of industrial catalysis. In the beginning of the 20th century, Fritz Haber, now famous

for the Haber-Bosch process that enables the production of ammonia from nitrogen and hydrogen, was looking for ways to improve his catalyst. [10] At that time, the best catalyst available for ammonia synthesis was manganese, while iron and nickel were slightly worse. As a catalyst, manganese did the job but there was still much room for improvement.

In a paper published by Haber and his colleague Le Rossignol in 1913, they describe their efforts and approach: "In our searching the elements for their capability to catalytically accelerate the formation of ammonia from its elements, we were led by the periodic table".[11] Their first plan was to go down in the column that contained manganese, but the periodic table was still empty there as technetium and rhenium were not yet identified at that time. So they needed a different approach. It was known that chromium, one place to the left of manganese, had similar catalytic properties. They started investigating tungsten, and even tried uranium, which turned out to be a "surprising success". After testing the elements located near manganese in the periodic table, their conclusion was that "both in the iron column as in the manganese column, the catalytic ability greatly increases with increasing atomic weight". In the end, Carl Bosch, working at BASF at that time and appointed to scale up the production of ammonia and design an industrial process, decided that the catalyst of choice would be iron, because it proved to be "particularly trustworthy and promising". Today, over a hundred years later, the Haber-Bosch process still uses iron catalysts, often mixed with small amounts of other metal-oxides such as potassium.[12]

This history shows that Haber and Le Rossignol first identified their starting point and from there on systematically tried different materials, which illustrates that they were led by certain trends in the materials they investigated. One trend they discovered was the increasing "catalytic ability" for ammonia synthesis as the atomic weight of the catalyst material increased. These trends in catalytic performance are nowadays thoroughly documented, and some of these trends are based on the so-called Sabatier principle. The Sabatier principle describes the binding strength of a reactant molecule to the surface of a catalyst, which depends on the adsorption energy of that specific reactant to that material. The best catalyst for a certain reaction binds molecules with an optimal strength. If the molecular adsorption energies are too low, the reactant molecules will not bind well enough to the catalyst and may not dissociate as a first step towards the reaction product. Also if the adsorption is too strong, reactions may be inhibited and, in addition, the catalyst surface will get poisoned rapidly with strongly bound reactant or product molecules. Different metals have different binding energies, and this effect is often displayed in graphs, showing the reaction rate versus the adsorption energy of different catalyst materials. Often, the shapes of these plots resemble a mountain, for example going from low via optimal to high binding energies, and they are referred to as 'volcano plots'. The material at the top of the volcano shows the best reaction rate and has the optimal balance between adsorption of reactants and desorption of products for that specific chemical reaction.

Research methods based on trial and error, similar to the approach followed by Haber and Le Rossignol, were common among scientists in the early 20th century. As technology developed further, more advanced techniques and methods to study catalysts became available, providing novel insights. The development of electron

microscopy in the 1930s allowed researchers to visualize their catalyst samples in unprecedented detail. In 1940, von Ardenne and Beischer published a paper in Angewandte Chemie, describing the power of transmission electron microscopy (TEM) and its use in catalysis research. They were able to show structural and morphological details of platinum, nickel, and iron catalysts, and investigate the support material.[13] To study the effect of real chemical reaction conditions on catalysts, scientists started to compare freshly prepared samples with samples that had been used for catalysis. For example, by using scanning electron microscopy (SEM), it became evident that platinum catalyst microparticles used for the gas-phase CO oxidation reaction changed significantly. On the initially smooth surface of the particle, large uneven protrusions had been formed after exposure to reaction conditions (i.e. high temperature and high CO pressure).[14]

This type of research, comparing the catalyst before and after the chemical reaction has taken place, is referred to as post-mortem analysis. Even though this approach cannot reveal all aspects of how the catalysts change their structure during the chemical reaction, it has served as a very valuable first step, for example providing insight in catalyst deactivation. [15] This has been useful in the design of new, improved types of catalysts.

1.3   TEM investigation on MoS$_2$ catalysts

In the work described in the first two chapters of this thesis, we used this traditional approach and implemented an additional feature. Using special TEM mixed mesh sample finder grids to support our catalyst sample, we were able to find back and image exactly the same areas of the catalyst before and after the sample was exposed to ambient air. We were able to determine the effect of ambient air exposure was on individual catalyst particles. As a catalyst, we studied (Ni/Co)MoS$_2$ supported on high surface-area γ-Al$_2$O$_3$.

(Ni/Co)MoS$_2$ catalysts are widely used for the hydrodesulfurization (HDS) of fossil fuel. The HDS reaction is a process designed to clean crude oil when it is converted into fuel: it is used to remove sulfur from the oil feed so that these contaminants do not end up in our atmosphere when the fuel is burnt.[16]

However, this approach to catalyst evolution leaves one of the most important question unanswered: What happens with a catalyst *during* the reaction? To answer this question, the experimentalist would need to apply elevated gas pressures and high temperatures, in order to provide conditions similar to those inside a genuine chemical plant, while the catalyst is being investigated for changes in structure and composition. These types of experiments, in which data are collected on the behavior of the sample during the course of the process, are called *in situ* experiments. When also the catalytic performance of the sample is evaluated by monitoring the composition of the gas that has been in contact with the catalyst, e.g. by using mass spectrometry, they are referred to as *operando* experiments.[17]

Early studies, combining traditional post-mortem TEM experiments on platinum catalysts with e.g. *in situ* Auger electron spectroscopy, a technique already available in the 1970s,[18] provided new insight in catalyst regeneration and emphasized the need for and value of *in situ* electron microscopy techniques.[19]

It could be argued that catalysts can also be studied under low-pressure and low-

temperature conditions, since the species involved in a catalytic reaction can have identical chemical potentials both under regular reaction conditions, i.e. the combination of a high temperature and a high pressure, and at the combination of a low, e.g. cryogenic temperature and a low pressure, e.g. ultra-high vacuum conditions (UHV, working pressure ~1.0×10^{-9} mbar). What is kept equal by changing temperature and pressure such that the chemical potentials remain the same, are all thermodynamic equilibria between the reactants, products and intermediate stages. This is very attractive, since the lower-temperature, lower-pressure conditions are usually much more accessible to high-resolution surface-science techniques. However, what this approach ignores is the important role of the kinetics in the investigated catalytic processes. There are two general ways in which the kinetics can bring the system so far out of thermodynamic equilibrium that keeping the chemical potentials unchanged is no guarantee for keeping the surface in the same structure and composition. The first is that in the dynamic situation of genuine reaction conditions, the combination of the reaction itself, the supply of the reactants and the removal of the products continuously keeps the reactants, the intermediate products and the final product(s) away from thermodynamic equilibrium with each other. The catalyst in its working state should be regarded as one of these intermediate products. It is evident that slowing down the kinetics may bring the system closer to thermodynamic equilibrium, but this will then bring it away from the truly active state of the catalyst. The other kinetics problem arises when the lower pressures that may be necessary for certain measurement techniques thermodynamically correlates with a temperature that is so much lower, that one or more steps in the catalytic process effectively comes to a standstill, simply because the associated activation energy is too high to be overcome frequently enough to reach equilibrium on a reasonable time scale. A typical example is the case where reactant molecules adsorb on a surface at cryogenic temperatures, after which 'nothing' happens, i.e. no bond breaking, no diffusion, no compound formation and no desorption. Obviously, this is not the equilibrium situation, but the time to reach equilibrium would be unacceptably long. There is no alternative, *in situ* and operando experiments are really needed.

1.4   *In situ* and operando TEM

Switching from traditional TEM experiments to catalytically more relevant *in situ* TEM is not trivial. The reason for this lies in the working principle of a transmission electron microscope, as schematically shown in Figure 1.1.

A beam of electrons is generated at the top of the microscope by the electron gun. This e⁻-beam travels down along the center of the column, meanwhile being manipulated by sets of electromagnetic lenses that are able to focus the electron beam at the sample. The sample is mounted on the tip of a holder which is introduced into the TEM column via a loadlock. The electrons transmitted through the sample continue downward, again being manipulated by electron lenses, and are finally detected by the CCD camera placed at the bottom of the column. Apertures are placed at several positions along the Y-axis to regulate the intensity of the e⁻-beam and to block out electrons traveling too far away from the optic axis, reducing the noise.
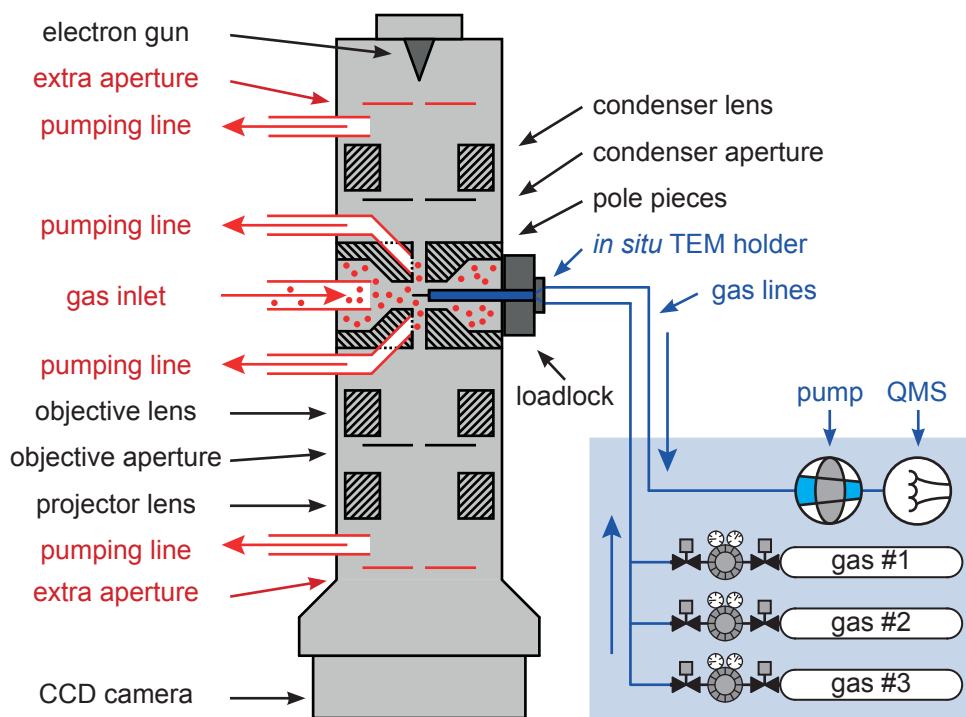
Figure 1.1. Schematic cross section of a transmission electron microscope, showing all the parts of a traditional TEM in black and gray, while the additional parts that make up an environmental TEM are shown in red. The gas flow equipment and gas lines that cover the *in situ* part are shown in blue, to the right of the TEM.

The electrons will be scattered by anything that is placed in between the gun and the camera. For that reason the column is constantly pumped down to a working pressure of $\sim 1.0 \times 10^{-7}$ mbar, thereby reducing unintentional scattering by collisions of electrons with gas molecules and enhancing the resolution of the image. This low pressure is also necessary for the electron gun, as this sensitive component is easily destroyed by any gas molecules that come into contact with it. Additional pumps placed next to the electron gun ensure a local pressure of below $\sim 1.0 \times 10^{-8}$ mbar. The sample that is loaded into the column via the airlock inherently also meets this low pressure environment. Imaging catalyst samples at higher pressures or even under reactant gas conditions therefore requires a different approach.

One way of realizing an elevated gas pressure at the sample while the rest of the TEM column remains at a reasonably low pressure is by using a differentially pumped environmental TEM (ETEM, Figure 1.1, parts outlined in red).[20-22] A gas feed is placed in the column of the ETEM, with the gas inlet placed directly next to the sample. The gas is inserted through the inlet and fills up the volume around the sample and sample holder, in between the pole pieces (Figure 1.1, red dots indicate gas molecules). To prevent the gas from diffusing too much to the rest of the TEM column, extra apertures are placed above and below the pole pieces. Main pumping lines are placed in the pole pieces to remove the majority of the gas, while extra

pumping lines above and below the pole pieces remove the diffused excess gas and thereby keep the pressure at the vulnerable electron gun low. This approach of additional apertures and differential pumping also increases the mean free path of the electrons in the column by reducing unintentional scattering.

The main drawback of this technique is the pressure range in which an ETEM can be operated. Despite the restricted volume that the gas is contained in, a too high gas pressure deteriorates the imaging resolution by scattering the electrons. This already occurs above a local pressure of 5 mbar, yielding blurred micrographs, while prolonged exposure to pressures above 50 mbar will destroy the electron gun.[20,23]

To overcome this restriction, a different approach was taken. Windowed cell systems were developed, which were able to contain both the catalyst sample and the reactant gases in a small volume, greatly reducing the electron path length through the gas layer. The cells, commonly referred to as nanoreactors, are currently available in a variety of versions.[24-30] The nanoreactors that were used in chapter 5 of this thesis consist of a single Si chip, prepared using MEMS technology (micro-electromechanical systems), containing gas in- and outlets that are connected by a narrow channel. To use the nanoreactors in a TEM, a dedicated sample holder was developed simultaneously, containing a pair of capillaries running from the base of the holder to the tip. The nanoreactor is placed on two O-rings in the tip to ensure a leak-tight connection with the capillaries. Tube fittings at the base of the holder allow connections to a gas flow system of choice, and to a mass spectrometer to analyze the exhaust gas. A more detailed description of the components, including images of both the nanoreactors and the TEM holder, can be found in sections 5.2.2. - 5.2.4. The pressure regime in which this specific combination of tools can be operated ranges from vacuum up to 14 bar, making it a suitable approach to study a broad range of catalysts under their industrially relevant conditions.

1.5   Operando TEM experiments of Co nanoparticles

Chapter 5 of this thesis describes the experiments that we performed using the operando TEM tools described above, showing atomic scale images of cobalt nanoparticles at 1 bar pressure and elevated temperature. Cobalt nanoparticles are used as catalysts in the Fischer-Tropsch process. This process, currently running commercially at an industrial scale worldwide, transforms a mixture of CO and H_2 gas into liquid hydrocarbons. These hydrocarbons can then be used as a renewable, synthetic fuel source, instead of traditional fossil fuel.

The cobalt nanoparticles were prepared via colloidal chemistry, allowing accurate control over the size distribution in which the resulting nanoparticles are synthesized.[31] This colloidal approach was also used to synthesize cobalt-rhenium bimetallic nanoparticles of varying composition. A thorough investigation of the cobalt-rhenium nanoparticles is described in chapter 4. A range of TEM techniques (scanning transmission electron microscopy - energy dispersive X-ray spectroscopy (STEM-EDX), high-angle annular dark field (HAADF) and regular HRTEM(-EDX)) was exploited to characterize the nanoparticles, revealing the atomic composition and distribution of the metals inside the particles.

1.6 Developments of other *in situ* techniques

The development of the traditional TEM into an instrument that is able to perform *in situ* and operando experiments is part of a broader progress. Inspired by early surprises in this field of research and supported by considerations such as those given in section 1.3, a growing number of instruments and measurement techniques is being made suitable for operation under catalytic reaction conditions.[32] As each individual technique and instrument only approaches the catalyst sample from a relatively narrow point of view, the results of single experiments show a rather limited part of the picture. Therefore, in order to fully investigate the catalytic process in all its aspects, it is essential to combine multiple approaches and apply different techniques on a catalyst sample.

Surface science laboratories, traditionally working with UHV setups containing surface sensitive equipment such as scanning tunneling microscopy (STM) and atomic force microscopy (AFM), have made vast progress by implementing small, high-pressure gas flow cells inside the UHV setup.[33,34] This approach allows flowing reactant gases over heated metal single crystal surfaces and observing the effect of these conditions on the metal surface. Recent publications reveal the power of these setups by yielding atomic-scale insight into catalytic reactions such as the Fischer-Tropsch reaction on a cobalt surface,[35] and CO oxidation and NO reduction on platinum.[36] X-ray techniques such as surface X-ray diffraction (SXRD) and X-ray absorption spectroscopy (XAS), traditionally limited to UHV conditions, are currently also being modified for *in situ* experiments, to acquire information about the geometrical structure, elemental composition and electronic structure of the surface.[37,38]. In some experiments, *in situ* X-ray techniques are used in direct combination with a second *in situ* technique to instantly benefit from both approaches.[39,40]

That also simpler and cheaper methods can be used to investigate surfaces under genuine catalytic conditions is illustrated by a recent investigation [41] in which we collaborated with Leiden Probe Microscopy [42] to design, build and apply a small, relatively simple tabletop flow reactor for catalytic experiments. The reactor uses the reflection of visible light over a metal single crystal to see the effect of different gas conditions and sample temperatures on the reflectivity of the sample surface. This optical experiment provides direct information on the interplay between different regions on a catalyst that are in different chemical states due to subtle differences in local conditions, e.g. local partial pressures. Such information complements the highly local information that is acquired through the TEM experiments that form the main subject of this PhD thesis. As was remarked above already, we can only gain a complete understanding of the complex mechanisms of catalysis by combining information of many different types, for example on many different length scales. In this thesis we concentrate on the atomic scale.

Next to all the scientific images and graphs, this PhD thesis contains additional illustrations, mostly dedicated to the instrumentation that was used for the conducted experiments. These include the cover page, the starting pages of all chapters and the upper corner of all right pages. A brief explanation of these illustrations is provided in a separate section near the end of the thesis.

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