Atomic-scale Study of a Hydrodesulfurization Model Catalyst

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Preface

This thesis is submitted to the Faculty of Science at the University of Aarhus, Denmark, in order to fulfill the requirements for obtaining the PhD degree in physics. The studies have been carried out under the supervision of Flemming Besenbacher in the scanning tunneling microscopy (STM) group at the Department of Physics and Astronomy from August 1998 to July 2002.

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During the thesis work, the author has contributed to the following published papers or papers in preparation:

[I] **Atomic-scale Structure of Single-layer MoS\(_2\) Nanoclusters**

[II] **Atomic-scale Structure of Co-Mo-S Nanoclusters in Hydrotreating Catalysis**

[III] **One-dimensional Metallic Edge States in MoS\(_2\)**

In preparation.

[V] **The Chemistry of One-dimensional Metallic Edge States in MoS\(_2\) Nanoclusters**
Submitted.

[VI] **The State of MoS\(_2\) Nanoclusters under Hydrotreating Conditions**
In preparation.
[VII] Atomic-scale study of Thiophene adsorption on MoS$_2$ Nanoclusters
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Chapter 1

Introduction

Catalysis plays an incontestable role in upholding the modern society by providing for example fuels, commodities, fine chemicals, pharmaceuticals, and means for a sustainable energy production. The impact of catalysis is probably best illustrated by the fact that products manufactured through catalysis account for about 10-15% of the gross national products of industrialized countries [1, 2], a number which is not likely to decline. Another prominent application of catalysis is concerned with the prevention of pollution. Societal concerns for preservation of the environment has driven the development of many specialized catalysis-based technologies, including the three-way catalyst effectively reducing pollution from car engine exhaust gasses, DeNOx catalysts for power plants and a wealth of processes upgrading and purifying fossil fuels for transportation. Belonging to the latter category, the hydrotreating catalyst is the main subject of this thesis and will be introduced after a more general introduction to heterogenous catalysis.

1.1 Heterogeneous Catalysis and Surface Science

In the vast majority of catalytic processes, reactants in either gas or liquid phase are catalyzed heterogeneously on the surface of a solid material. For a given chemical reaction, the surface of the heterogenous catalyst offers an alternative and energetically favorable reaction pathway for the reactants, in which one or more activation barriers are low compared to the uncatalyzed reaction in gas or liquid phase (Fig. 1.1). On the microscopic level, the heterogeneously catalyzed process proceeds by a series of elementary steps, including the adsorption of reactants on the active surface of the catalyst material, breaking or weakening of adsorbate bonds, adsorbate diffusion and reaction to form products, followed by desorption to regenerate the active site on the surface. The catalyst does not alter the thermodynamics of the reaction, nor is it consumed during the process.

The keyword in understanding heterogeneous catalysis is the surface of the catalyst material since the chemical transformations takes places here. The reactivity of a heterogenous catalyst scales directly with the number of exposed active sites on the surface. In technical catalytic systems this is optimized by dispersing the active material, often consisting of sev-
Gibbs free energy, $G$

Reaction coordinate

Figure 1.1: Schematic illustration of a surface-catalyzed reaction. The uncatalyzed gas-phase reaction (dashed line) is highly activated. The alternative path offered by the catalytic surface involves several, but less activated reaction steps, which are indicated with legends.

eral compounds, as nanometer-sized particles onto highly porous oxide or carbon supports with surface areas often in excess of 500 m$^2$/g (see Fig. 1.4). Often, the actual size and shape of the nanoparticles also determine the reactivity of the materials. This structural complexity of the materials combined with extreme reaction conditions reaching temperatures of several hundred degrees Celsius and pressures up to hundred bars are factors limiting the possibility of achieving a detailed structural characterization, explaining why catalyst development has primarily been based on empirical experimentation.

It is a striking fact that present day catalytic processes have been developed almost without exceptions through costly trial-and-error experiments. In many respects, heterogeneous catalysts have been treated as black boxes only characterized by their qualities in terms of reactivity, selectivity and stability with a poor understanding of the underlying mechanisms. In order to understand the macroscopic behavior of catalysts it is necessary to focus on the detailed atomic structure and fundamental microscopic processes of catalysis. Through the recent development of new and better catalyst characterization tools it has become possible to study the fundamentals of catalysis, and a fairly good understanding has thus been obtained for some systems [1, 2]. Today, the growing interest in advancing to more selective and energy-efficient catalytic processes, has motivated researchers in fundamental catalysis even further [3]. The ultimate goal of rational catalyst development is to achieve full understanding and control of the constituents at the molecular and atomic levels. With this ability, it will be possible to construct tailor-made, high-performance catalysts for even highly specialized chemical reactions, with obvious benefits for the chemical industries and, not least, the everyday consumers of the countless products relying on catalytic processes.

To approach a detailed atomic-scale understanding of the heterogeneous catalysts, problems are attacked in surface science studies of well-characterized model systems [4, 5].
Within this surface science context, the complexity problems are stepwise broken down into pieces by adopting a simplified approach. The active materials are typically represented by idealized single-crystal surfaces kept under ultra-high vacuum conditions (pressure below $1 \times 10^{-10}$ mbar). This allows for a detailed characterization of the surface structures by the whole arsenal of surface analytical tools. Such fundamental and idealized studies have provided valuable information on a number of catalytic systems with the most prominent example being the synthesis of ammonia ($\text{NH}_3$) on an iron-based catalyst. Despite the great complexity of this system, the mechanisms of this important catalytic process have essentially been solved on the basis of surface science modelling [1, 6]. Detailed surface science investigations have also recently been able to guide the development of new and better catalysts [7, 8]. Surface scientist have thus come a long way in understanding the basics of catalysis, but concerns are, however, that additional and essential insight is often lost in the highly idealized studies of single crystal surfaces. In order to describe the disparities between the surface science approach and real complex catalytic systems operating at high temperature/pressure, two phenomenological gaps have been identified and termed the pressure gap and materials gap, respectively.

The pressure gap is concerned with the order-of-magnitude difference between typical operating conditions (1-100 bar) and the range of pressures ($10^{-16}-10^{-5}$ mbar) in which most surface analytical techniques are functional. Under the idealized conditions, the high-pressure situation is imitated by exposing surface structures to a high incoming flux of molecules to facilitate high adsorbate coverages. It has been shown by careful consideration that UHV data in some cases can be extrapolated the results to high pressures [9, 10], but it is not clear to which extent this is of general validity.

The materials gap covers the disproportion between the supported catalytically active clusters and the corresponding model system. A description based on studies of single-crystal surfaces may work very well (and has often proven to do so) but only if the nano-clusters in the real catalyst exposes the same facet at in the model and if this facet, in reality, is the active part of the cluster. In some cases (as the one in this thesis) the properties of the catalytically active material in the form of nanoclusters behave quite differently from those obtained from the bulk material, and geometric or electronic features in the microscopic clusters turn out to be controlling the reactivity on the macro-scale. A fully functional oxidation-catalyst consisting of $\text{TiO}_2$-supported Au nanoclusters is one good example of how the properties of the materials may change as the dimensions are reduced, since bulk Au is know to be noble and notoriously inert [11]. Hence, in order to bridge the materials gap, it is desirable to investigate new and more realistic model systems, i.e. consisting of particles on flat supports.

Adding to the complexity is the fact that the pressure and materials gaps are sometimes interrelated. This occurs when the morphology or surface composition of the active material depends on the composition of the ambient gasses. One recent example is the dynamic shape changes of nanocrystalline Cu/ZnO observed when switching between oxidizing and reducing gas-compositions [12, 13]. Ideally, such gas-induced structural changes should be observed in situ and for that purpose many new and promising techniques exist [14–16]. Alternatively and less demanding, suitable model systems, investigated under UHV and up

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1Characterization under relevant reaction conditions, i.e. high pressure and temperature
to the moderate pressures where most surface science techniques work excellently, may be used to examine gas-induced structural or compositional changes by “quench-and-look” experiments.

Aside from the fact that realistic model systems are difficult to assemble, most surface science techniques based on electron diffraction or spectroscopies are averaging techniques where the information about individual particles is lost and consequently these techniques have a limited applicability for analyzing complex model systems consisting of e.g. nanoclusters. This currently makes the attempts to bridge the materials gap a large challenge to researchers. Scanning Probe Techniques, such as the scanning tunneling microscope (STM) and its cousin, the atomic force microscope (AFM) [17], stand out as indispensable tools for such studies owing to their capability of achieving atom-resolved real-space images of localized regions of the surface such as nanoclusters. The STM has provided much information on the structures and electronic properties of surfaces [18–22], and since it also resolves signatures of adsorbed particles it has become an outstanding tool for monitoring chemical reactions on surfaces [23]. In particular, the exceptionally high resolution of STM makes it possible to address catalytically active sites directly on the atomic level [24, 25]. Furthermore, studies of catalyst model systems with STM also show promising progress in the attempt to narrow the pressure gap that exists between the ultrahigh vacuum conditions and real catalytic process conditions. In several studies it was possible to image, in atomic detail, single-crystal surfaces at ambient pressures. Such in situ model catalyst studies have already provided much insight into the significance of the pressure gap [9, 26, 27].

1.2 Hydrotreating

The subject of this thesis is the hydrotreating catalyst. The industrial application of hydrotreating catalysts is in the wealth of processes applied to upgrade and process crude oil to comply with current technological and environmental standards. Hydrotreating processes are reductive hydrogen treatments of the organic molecules comprising crude oil, to remove hetero-atoms like nitrogen, oxygen or sulfur. The purpose of removing such impurities is twofold. The burning of S and N containing fuels presents a severe threat to the environment, i.e. the formation of acid rain from SO\textsubscript{2} or NO\textsubscript{x} emissions. Additionally, other transition-metal based catalysts treating the crude oil fractions generally have a very low tolerance against impurity atoms like S, and if untreated, the sulfur leads to an accelerated deactivation and breakdown of the catalyst.

The hydrotreating catalyst is an excellent example of a technical catalyst which has undergone a dramatic increase in performance as new and better characterization tools have been developed. In fact, in the early 80’s it was the general feeling in the industry that the hydrotreating catalysts could not be developed further. It soon became clear that new detailed insight obtained by catalyst characterization studies would lead to new ideas for catalyst preparation and trigger a dramatic increase in the efficiency. Undoubtedly, the steep descent of the SO\textsubscript{2}-emission curve in Fig. 1.2 can be explained by the emergence of improved in situ catalyst characterization tools, which have changed the way in which catalysts are be-
1.2 Hydrotreating

Figure 1.2: (a) The reduction of SO₂ emissions from fossil fuels facilitated by the implementation of improved hydrotreating processes in the end of the last century [28]. (b) Table with typical sulfur and nitrogen impurity levels of crude oils with different geographical origin [29].

- **Type** | **Sulfur (wt%)** | **Nitrogen (wt%)**
- Arabian Light | 1.8 | 0.1
- Arabian heavy | 2.9 | 0.2
- Attacka | 0.07 | <0.1
- Boscan | 5.2 | 0.7

Today, the traditional catalyst characterization techniques which have provided this insight [2, 5], however, seem to have reached a limit in terms of obtaining the desired insight into the atomic-scale structure of the hydrotreating catalysts. This coincides with the new, severe legislation pressing refiners to further upgrade and purify the oil feedstocks and thus catalyst manufacturers to improve the performance of the catalytic processes. Especially the hydrodesulfurization (HDS) reaction is subject to increased attention, since new legislation in the European Union and the U.S. has imposed severe limits on the impurity levels in transport fuels. The new specifications for e.g. diesel require that the amount of sulfur is reduced from 350 ppm to better than 50 ppm by 2005 [29–31]. While these limits are mainly set by environmental requirements, additional economic and technological factors associated with the catalytic upgrading of, in particular, heavy fuel oil fractions, push the demands for catalytic performance even further. In so-called *deep* hydrodesulfurization, the aim for the next decade is to go below 10 ppm of sulfur.

These stringent demands call for catalyst manufacturers to improve the catalytic performance further. This has motivated a lively activity in the field of hydrotreating catalysis. Especially within surface science, researchers have taken up the challenge to elucidate the fundamental operation-mode of the hydrotreating catalysts on the atomic scale using all available techniques both from an experimental and theoretical point of view. Due to the very complex atomic composition and structure of the catalyst this, however, presents a big challenge, and in previous studies important aspects of morphology, atomic-scale structure, and position of active sites have only been suggested indirectly, simply due to the lack of appropriate characterization tools. As mentioned in the general introduction, the STM has entered the catalysis arena as an excellent tool to solve such issues. However, whereas the conventional single crystal approach may work well for metals, it is not very suitable for the study of the activity and structure of hydrotreating catalysts, since it will become clear that the reactivity is uniquely associated with sites at the *edges* of active nanoclusters. Consequently, new and innovative ideas are needed in order to narrow down this materials gap.

In this thesis, novel atomic-scale information, acquired in studies with the Scanning...
Tunneling Microscope (STM), will be presented on the hydrotreating catalysts. Using a new synthesis method, a model system of supported MoS$_2$ nanoclusters has been developed, with characteristics similar to the active nanoparticles in a real hydrotreating catalyst and accessible to direct atomic-scale imaging with an STM. By investigating the clusters in atomic detail, a hitherto unprecedented view of the catalyst structure and reactivity has been achieved. Thus, the results bring model studies of hydrotreating catalysts one step closer to the real world, and have already received massive international attention [3, 32–38]. To put the present work into perspective and explain the present state of insight into structure and reaction schemes, a short account will be given in the following sections introducing the hydrotreating process together with earlier experimental results characterizing the HDS catalyst. This will pinpoint the many fundamental questions related to the catalyst structure and motivate the STM studies presented in this thesis.

### 1.3 Hydrodesulfurization

The hydrotreating catalyst is remarkably versatile, in the sense that it can, simultaneously, be applied to clean up S, N and O impurities imbedded in the organic molecules comprising crude oil. Although there are some technical variations in the processes by which the hetero-atoms are removed, the fundamental principles appear to be the same, and in the present introduction the hydrodesulfurization (HDS) reaction serves as an excellent example to illustrate the process. Recently, attention has indeed mainly been focused on the ability of the catalysts to remove sulfur, thus justifying the HDS as the starting point for the catalyst model studies [29, 39].

In the HDS reaction, sulfur impurities imbedded in carbon molecules are removed by trickling a mixture of the crude oil fraction and gaseous hydrogen through a catalyst bed at an elevated temperature and pressure. This is schematically illustrated in Fig. 1.3. In this way, the sulfur hetero-atom is reduced by the hydrogen and released from the organic molecule as gaseous H$_2$S.

The catalyst technology bridges many length scales from the large-scale reactor through macroscopic catalyst pellets down to the actual chemistry occurring on particles with typical dimensions on the nanoscale (see Fig. 1.4). The alumina ($\gamma$-Al$_2$O$_3$) support is the backbone of the HDS catalyst. The role of this robust and highly porous carrier material is primarily considered to support the active nanoparticles on a large surface area and hereby ensure good contact with the reactants. On the smallest scale, the active phase of the basic catalyst consists of MoS$_2$ particles promoted with small amounts of Ni or Co and is referred to as CoMoS structures$^3$. These nanostructures are the ones of principal interest in the quest for a better insight into the catalyst.

Technologically, the preparation of the HDS catalyst is a major issue, and the actual technique has decisive influence on the ultimate performance [42, 43]. Usually, the catalyst support is impregnated with specially selected Mo-oxide compounds and a whole range of additives, and subsequently sulfided inside the reactor into the structure outlined above.

$^3$MoS$_2$ promoted with Ni is sometimes referred to as NiMoS, but is believed to have the equivalent basic structure of CoMoS. [41]
1.3 Hydrodesulfurization

The feed which is to be hydrotreated is normally very inhomogeneous, and this puts large demands on the performance and versatility of the catalyst to ensure a homogenous output. Depending on the geographical origin of the crude oil, the feed contains varying amounts of sulfur in terms of weight percent (see table in Fig. 1.2b). Also, with the oil feed being the result of decaying fossil organic materials comprising the oil, the diversity of the molecules entering the HDS reaction is large, ranging from simple organosulfur molecules like thiols (R-SH) or thiophenes to more complex molecules with the heteroatom deeply imbedded inside a molecular carbon surrounding.

Typical operating conditions of the catalyst are at temperatures in the range between 300 °C to 400 °C and a hydrogen pressure between 10 to 70 bar, but the precise operating conditions are dictated by the composition of the specific oil fraction. Especially heavier oil fractions, which generally contain more complicated molecules, have a lower reactivity and need forced HDS conditions. These deep HDS capabilities of the catalyst currently receive much attention, due to the persistent demand to reduce the S content in heavy oil fractions.

At present, the legal requirements regarding fuel specifications can in principle be fulfilled, but only at considerable economic expense. The limit it set by the hydrogen consumption, which is a rather expensive resource. Also the integrity of the catalyst puts limits on the performance. At elevated temperatures unwanted side reactions (reduced selectivity) may be initiated resulting in a more rapid aging due to sintering or coking. In order to optimize a large-scale industrial process like hydrodesulfurization according to future demands
Figure 1.4: A sketch illustrating the scale involved in the catalyst technology of hydrotreating. From the left: Inside a typical large-scale reactor the catalyst material is present as \( \gamma \)-Al\(_2\)O\(_3\) pellets which support a robust and porous texture of the catalyst. Onto these the active MoS\(_2\)-like nanoclusters are typically deposited by wet-chemistry impregnation, thus sustaining a high contact area to the reactants which flow in the pores of the catalysts support. On the smallest scale (\( \sim 1 \) nm), active sites on the clusters are responsible for the actual chemistry of the catalytic reaction.

and to achieve an economically feasible operation, it is evident that improvements have to be carried out with respect to both process conditions, reactor configuration and catalyst preparation. In this thesis emphasis will only be on the last of these aspects, i.e. a study of the atomic-scale structure of the active catalyst nanoparticles.

1.4 Catalyst structure and reactivity

During the last three decades, the hydrotreating catalyst has been extensively characterized using a large variety of different tools, and several extensive reviews on the subject exist [29, 39, 42–44]. A complicating factor in obtaining a substantiated description of the catalysts lies in the inherent complexity of the system, rendering a complete investigation an enormous task. Only by using highly specialized techniques has new insight been attained.

A considerable effort has been aimed at relating fundamental macroscopic properties such as catalyst activity and selectivity to microscopic properties, i.e. catalyst composition, electronic structure and geometric structure. Especially, in situ extended x-ray absorption fine-structure spectroscopy (EXAFS) studies of the catalyst have given information on the composition, the average local coordination and interatomic distances of individual types of atoms in the catalyst particles. It is found that the active phase is present as MoS\(_2\)-like particles with a size of 10 - 20 Å [45–47]. For that reason, unpromoted MoS\(_2\) clusters are normally considered as starting point for models of the catalyst.

MoS\(_2\) is a layered compound consisting of S–Mo–S slabs held together by weak van der Waals forces. A unit cell of the MoS\(_2\) structure is illustrated in Fig. 1.5(a). Each slab
consists of a tri-layer with two close-packed hexagonal (0001) planes of S atoms and an intermediate hexagonal plane of Mo atoms, which are coordinated in a trigonal prismatic fashion to the six surrounding S atoms. In nature, pure MoS$_2$ (molybdenite) can be excavated and is normally encountered as the allotrope 2H-MoS$_2$ [48], which is a lamellar compound with the unit cell containing two S-Mo-S slabs stacked in an alternating fashion as illustrated in Fig. 1.5(b).

In the catalyst, the MoS$_2$ crystallites are believed to grow as slabs with relatively large dimensions parallel to the (0001) basal plane compared to the height perpendicular to the basal plane [29, 50, 51]. The traditional catalyst consists primarily of non-stacked two-dimensional (i.e. single-layer) structures. Stacked crystallite structures are, however, also observed in the catalyst at elevated sulfidation temperatures. In fact, catalysts prepared at higher temperatures are generally observed to have increased deep HDS capabilities, and it has been suggested that the modified reactivity of these is related to stacked three-dimensional clusters. These structures are termed type II structures, in contrast to single-layer type I structures [29, 52].

It has long been realized that the basal plane of MoS$_2$ is catalytically very inactive, and hence that the activity in the HDS process is somehow associated with the edges terminating the clusters [29, 53, 54]. Since the morphology of the cluster ultimately determines the nature of the exposed edges, the shape is a very important aspect in understanding the reactivity of the catalysts. Unfortunately, due to the amorphous and non-planar nature of the $\gamma$-Al$_2$O$_3$ support and the small size of the clusters, a detailed characterization is beyond the reach of, for example, high resolution transmission electron microscopy (HRTEM) [55]. Hence, very little knowledge of the cluster morphology exists.
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Figure 1.6: Ball model of a hexagonal MoS$_2$ cluster, obtained from a simple bulk truncation. **Left:** The cluster is oriented with the (0001) basal plane in parallel with the paper and it exposes the two different fundamental, low-index edge terminations. **Right:** Side view of the edges. The Mo atoms (blue) are coordinated to six sulfur atoms (yellow) at the S edge, whereas at the Mo edge the coordination to sulfur is only four.

1.5 Promoted catalyst structure: The CoMoS model

Upon adding Co in the preparation of the MoS$_2$-based HDS catalysts, a considerably more reactive (order of magnitude) catalyst is obtained. The origin of the effect of Co in the catalysts has been the subject of an extensive debate, a fact which is related to the above-mentioned difficulties in obtaining direct atomic-scale information on the catalyst structure. Since it has been established that small amounts of Co can dramatically change the reactivity of the catalysts, the Co is considered to be a **promoter** rather than a catalyst in its own right. Various models have been proposed for the promoted structure [29, 56, 57], but recently the discussion seems to have converged and there is general agreement on the so-called CoMoS model, which was originally proposed by Topsøe, Clausen and coworkers [52, 58, 59].

Structural insight into the promoted structures has been achieved by a combination of analytical techniques and activity measurements of e.g. thiophene HDS. Especially EXAFS, Mössbauer emission spectroscopy (MES), x-ray photoelectron spectroscopy (XPS) and infra-red spectroscopy (IR) have been successfully applied in *in situ* studies, and have provided information on the CoMoS catalyst. This has resulted in the CoMoS model (Fig. 1.7), where Co is found in three different phases, all co-existing in the catalyst during operation:

- **Co:Al$_2$O$_3**. Co atoms are dissolved in the alumina support
- **Co$_9$S$_8$**. The thermodynamically stable cobalt sulfide.
- **CoMoS**. A bimetallic sulfide-compound of Co, Mo and S. The compound has an MoS$_2$-like texture, into which Co atoms are incorporated. The phase is non-stoichiometric with respect to the Co/Mo ratio, and no unit cell can be defined in the crystallographic sense.

Of the three phases, only the last CoMoS structures are associated with an appreciable catalytic activity, and is therefore the structure of prime interest. In the structural model, the
CoMoS clusters are described as being essentially MoS$_2$-like, but with additional Co atoms embedded into the MoS$_2$ lattice at the perimeter of the cluster. It is proposed that Co atoms located at edge positions create new and more active sites. The promoting role of Co is, however, still extensively discussed, and the exact location of Co has not been identified. A prerequisite for a thorough elucidation of this seems to be a better understanding of the morphology and atomic-scale structure of CoMoS clusters.

### 1.6 Fundamental questions

Despite the enormous number of studies of HDS catalysts, many fundamental questions remain unsolved at present. Most of them are directly related to the fact that the traditional spectroscopic techniques, which have provided much insight into the nature of the catalytically active particles, are not able to unequivocally map the real-space atomic structure.

For instance, what is the preferential shape of the crystallites? One can speculate on the equilibrium shape of the crystallites in terms of the MoS$_2$ crystal structure. A ball model of a hypothetical, hexagonal, single-layer cluster following the stoichiometry of MoS$_2$ is depicted in Fig. 1.6. The hexagon is terminated by the two different, low-index edge-terminations of MoS$_2$, the (1010) Mo edge and the (100) S edge. The actual shape of the single-layer MoS$_2$ cluster is in principle governed by the relative stability of these two different low-indexed edge terminations. Depending on the exact edge free energies of the Mo and S edge, single-layer clusters can thus adopt shapes either as hexagons if they are of equal stability, as truncated structures with the most stable edge-termination dominating or, ultimately, as triangles terminated exclusively by one type of edges. In the 2H-MoS$_2$ bulk...
stacking sequence, alternate layers will expose Mo and S edges. One would thus expect the multi-layer type II clusters to grow preferentially in a perfect hexagonal morphology, since differences in edge free-energies tend to cancel between layers. These are issues which can be addressed in STM studies on suitable model systems.

The location of the active sites is strongly suggested from single-crystal studies demonstrating the outspoken inertness of the (0001) basal plane of MoS$_2$ [53, 54, 60] and infrared absorption spectroscopy (IRAS) of chemisorbed probe molecules like CO, NO or O$_2$ [29, 50, 61]. In all cases, the studies have pointed to positions at the edges of the MoS$_2$ clusters. But what is actually the detailed atomic-scale structure of the edges? And what are the active sites and exactly where on the edges are they located? Previously, the edge structure has largely been modelled from the bulk structure of MoS$_2$ (Fig. 1.6). However, due to the changed coordination of the edge atoms, reconstructions of the edges are likely to occur. Obviously, here a detailed understanding of the edge-structure is essential – an understanding which can only be attained by local probes such as the STM.

In a simple model, sulfur vacancies created at the edges of the clusters are considered to be the active sites for HDS [29, 62–64]. Evidently, such coordinatively unsaturated sites (CUS) will be prone to interact strongly with sulfur from organic molecules. The vacancies are thought to be provided by a reaction with hydrogen, which strips off sulfur from the edges. This can schematically be represented in this way [65]:

$$H_2(g) + S - \star \rightleftharpoons H_2S(g) + -\star$$ (1.1)

where the $\star$ denotes a sulfur vacancy at the edge. While in many studies the number of vacancies at edge sites (or corner sites) is considered to be a key measure of the catalytic reactivity, it is, however, noteworthy that the exact nature of such sites is far from established. Especially, the structural configuration of the vacancy is debated, i.e. will vacancies form preferentially on the Mo or the S edges of MoS$_2$, or maybe even on both?

Also the manner in which hydrogen enters the reaction with the S-bearing molecules is not yet known. At some step, hydrogen gas is believed to adsorb and dissociate on the catalyst particles. It has been suggested that besides creating vacancies through reaction 1.1, sulphydryl (S-H) groups are created on the catalyst, but the exact location or role of these is unknown. It is speculated that the adsorbed hydrogen may be released at some point to enter a hydrogenation of adsorbed species.

Similarly, the adsorption mode(s) of sulfur-bearing molecules on the catalytic clusters is controversial, and the literature contains plenty of suggestions for the mechanisms governing the adsorption of typical molecules found in crude oil. Possibly due to the diversity of such molecules in crude oil, a detailed understanding of the interaction with the catalyst particle remains a disputed issue. It is, however, clear that the molecules become hydrogenated and that the C-S bond is broken at some step, possibly in a direct interaction with S-H groups and/or vacancies.

The action of the MoS$_2$-based catalyst is to lower the activation barrier associated with one or possibly more of the reaction steps mentioned above, each of which, in principle, could be rate limiting. In order to work purposefully towards an improvement, it is of paramount importance to be able to pinpoint any rate limiting steps. Again, these are issues which can be approached in STM experiments resolving features of reaction intermediates.
For the CoMoS phase, the whole list of fundamental questions can be repeated, i.e. important fundamental questions exist concerning the effect of promoter atoms on the cluster morphology, atomic edge structure, active sites, etc. Especially the location of the promoter atoms imbedded at the edges of MoS\(_2\) clusters is disputed. The ternary CoMoS phase is non-stoichiometric and thus has no thermodynamically stable counterpart. It has, however, been established both experimentally [52, 66] and theoretically [67] that the CoMoS phase can be formed independently of any support, and it should thus be possible to form CoMoS clusters and study them independently.

In the literature it is suggested that the number of sulfur vacancies is the main factor controlling the catalytic activity. This is mainly based on a number of studies dealing with trends in the hydrodesulfurization of transition-metal sulfides (TMS), studies which have pointed out that the catalytic activity follows variation in the cohesive properties of the bulk TMS material. Experimentally, Pecoraro and Chianelli found a volcano-plot type of curve when correlating activity with the formation energy of the TMS normalized per metal atom. An optimum activity is found for RuS\(_2\) and OsS\(_2\) which have an intermediate heat of formation\(^4\). Refined theoretical approaches have recently been implemented, to further explain the variation in activity of the TMS [68, 69], and they all support that sulfur vacancies play a decisive role. In particular, Nørskov et al. [70] found the trend in HDS activity to follow the variation in the calculated sulfur-binding energy for different TMS, so that a weak sulfur bond correlates with a high activity. Specifically, it is shown for Co-promoted MoS\(_2\) that the promotional effect could be explained by a reduction in sulfur-binding energy and thereby an increase in the overall number of S vacancies. These studies are, however, based on the bulk properties of the materials, and although nice correlations are found, they neglect important structural parameters related to the cluster properties, which may in the end turn out to be controlling the activity. To obtain a more realistic description and capture the details, structures exposing the edges directly must be investigated.

### 1.7 New model catalyst studies

It is clear that the present picture of the working HDS catalyst is incomplete and that a gap exists between the insight obtained with the traditional catalyst characterization tools and the atomic-scale information essential for a deeper understanding. The catalysts have thus been treated in countless model studies applying the whole arsenal of spectroscopy- and microscopy-based surface science techniques. To address the unsolved issues, model studies have been performed on single-crystal surfaces under well-defined vacuum conditions, e.g. on MoS\(_2\)(0001) [53, 71, 72], Mo(110) [73–76], Mo(100) [77–79]. Although there is a lot to learn from such studies, they have not provided a major breakthrough in the microscopic understanding of the hydrotreating catalysts. It is especially difficult to relate the information of single-crystal studies to the real catalysts, since the reactivity is exclusively associated with sites on the edges of single-layer MoS\(_2\) nanoclusters. This problem is essentially the materials gap in hydrotreating catalysis, where one is left in a situation where the real world is too complex and the idealized model system is too simple. Hence, in order

\(^4\)For economic reasons these sulfides are not used in industrial HDS catalysis, since MoS\(_2\) has the best cost/performance ratio.
to start building a logical and seamless bridge over this gap, more complex model systems, capturing the essentials of the technical catalysts, need to be investigated.

In the group of Niemantsverdriet, hydrotreating model catalyst systems are synthesized by impregnating and spin-coating Mo and Co precursor compounds onto flat discs with an oxidic layer as support, a process much like real catalyst preparation. Subsequent sulfidation results in the formation of CoMoS or MoS$_2$ particles and provides a very powerful system for characterization with x-ray photoelectron spectroscopy, systematic studies of catalytic reactions, and for trying out new ideas in the synthesis [80–82]. However, no studies on the structure of the catalyst particles in the model system have been reported, making it difficult directly to elucidate structure-activity relations.

In this thesis, a “bottom-up” approach is taken where a model system is synthesized with starting point in the vast amount of knowledge generated on surface structures in fundamental surface science studies. It will be demonstrated how ~ 30 Å wide MoS$_2$ and CoMoS nanoclusters can be synthesized on an inert Au(111) substrate to form realistic model systems of the HDS catalysts, and how STM can be applied to scrutinize the atomic-scale structure of the catalyst particles.

1.8 Outline of the thesis

The long list of unanswered fundamental questions regarding the structure of the active MoS$_2$-like nanoclusters has been the main motivation for the present study and serves essentially as an outline of the thesis:

In Chapter 2 the experimental implementation of the scanning tunneling microscope will be introduced. It is important to emphasize that STM images in general reflect a convolution of electronic and geometric structure, and the basic theory behind the interpretation of STM images is given. Furthermore, a determination of the chemical identity of the observed features in STM images frequently requires assistance from other techniques. In this study, theoretical calculations have provided such insight in terms of STM simulations, and some of the concepts and elements of the interplay between STM experiments and theory will therefore be treated.

Chapter 3 is devoted to the synthesis of a novel HDS model catalyst consisting of gold-supported MoS$_2$ nanoclusters. The basic experimental principles concerning the preparation of the model substrate, the deposition and subsequent sulfidation of Mo into MoS$_2$ nanostructures on the Au(111) support will be presented. Basic properties of the model system will then be established to form the foundation of the rest of the thesis.

In the Chapters 4 to 8 the new pieces of information on the HDS catalysts obtained by atom-resolved STM are presented. Chapter 4 deals with the important issue of MoS$_2$ cluster morphology, atomic structure and in particular the nature of the edges terminating the cluster. Additionally, scanning tunneling spectroscopy (STS) reveals subtle electronic effect localized at the cluster edges. This chapter is based on the results of paper [I] and paper [III].

In Chapter 5, the interaction of the MoS$_2$ clusters with hydrogen is treated, and the first images of active sites in the form of S vacancies are presented. Thiophene (C$_4$H$_4$S) is in Chapter 6 introduced to test the interaction of the model system with a typical S-containing
molecule. When the clusters are pre-activated with hydrogen, thiophene is found to adsorb at unusual sites which leads to hydrogenation and bond cleavage of the molecule, i.e. the first step of HDS. The contents of these two chapters are based on paper [V].

In Chapter 7 the model system of MoS\(_2\) clusters is extended to also include the effect of the composition of the ambient gas. Synthesis of MoS\(_2\) clusters in a mixture of dihydrogen-sulfide (H\(_2\)S) and hydrogen (H\(_2\)) gas is shown to have marked impact on cluster shape and edge terminations. The synthesis-gas composition mimics the conditions of the working catalysts and the STM results may thus reveal the state of MoS\(_2\) in the real catalyst.

Chapter 8 treats the effect of Co promoters. An extension of the unpromoted system by co-deposition of Co leads to the formation of CoMoS clusters. The promoter is found to have a marked influence on cluster morphology and edge terminations due to a preference for Co to be located at a certain type of edge. Atom-resolved STM images provide information on the location of Co in the promoted particles, and the adsorption of probe molecules onto the CoMoS clusters reveals new insight on the role of the promoters. Some of the results are also presented in paper [II]. In Chapter 9 the results summarized and proposals for new directions in the investigations of hydrotreating model catalysts are given.
Chapter 2

Scanning Tunnelling Microscopy

The results presented in this thesis demonstrate how atomic-scale information on the structure of surfaces and clusters synthesized on these can be obtained with the scanning tunnelling microscope (STM). In the present chapter, a detailed description of the principles and concepts of scanning tunnelling microscopy will be given together with a description of the experimental implementation used in this thesis. The basic elements, theories and applications of STM are treated extensively in a number of textbooks [83–86].

2.1 Principle of scanning tunneling microscopy

The fundamental principle of STM is quite simple. By approaching an atomically sharp metal (typically W) tip into close proximity (≈ 5 Å) of a surface, electronic wavefunctions of the tip and surface will start to overlap. This enables electron exchange in the vacuum gap between the tip and surface, i.e. the phenomenon described in quantum mechanics as tunneling. For the conduction electrons at the Fermi level, the vacuum gap constitutes an energy barrier of approximately the average magnitude of the work functions of the tip and surface and a width corresponding to the tip-sample separation. If a small bias voltage ($V_t$) is applied across this tunnel junction, the Fermi levels of the tip and sample are shifted relative to each other, allowing for electrons to tunnel elastically from filled sample states into empty tip states (or vice versa depending on $V_t$), i.e. resulting in a net tunnel current.

In the usual mode of operation the tunneling current is monitored while the STM tip is raster-scanned across the surface at a fixed bias voltage using a piezo-robot to control the $x$-$y$-$z$ motion of the tip (Fig. 2.1). While the tip sweeps over surface structures, a feedback circuit regulates the tip-sample separation in such a way that the tunneling current is kept at a constant preset value (typically in the nA range). In this so-called constant current mode, the $z$ position of the tip (or, in reality, the feedback signal) is stored as a function of the lateral coordinates of the tip, to produce a topographic STM image of the surface corrugation beneath the tip. Alternatively, the STM may be operated in the constant height mode, where the $z$-position is kept constant and direct variations in the tunneling current are recorded as surface corrugation. Generally, constant current operation yields better resolution, whereas
The constant height mode allows faster data acquisition.

The ability of the STM to achieve atomic resolution on the sample is in a simple way explained by a strong exponential dependence of the tunnel current on the actual tip-sample separation ($z$). One can estimate that a shift in tip-sample distance of only 1 Å results in an order of magnitude variation in the tunnelling current ($I_t$). This means that ideally the entire tunnel current is localized in the junction between a single atom protruding from the tip and the sample, thereby making atomic resolution intuitively plausible, see Fig. 2.2.

### 2.2 The Aarhus Scanning Tunneling Microscope

Although conceptually simple, the actual realization of an STM apparatus is a great challenge. The typical tunnelling distance of less than 10 Å requires that the tip is placed with sub-Angstrom precision using construction elements on the centimeter scale, i.e. a size mismatch spanning almost 9 orders of magnitude. Also the extreme sensitivity of the tunnel current towards even minute variations in the tip-sample distance, which is exploited during STM operation, means that outside vibration must be eliminated through the appropriate isolation. The construction of an STM is thus a formidable task, but today the technical difficulties have largely been overcome and STM instruments are built which can routinely provide atomic resolution on surfaces [87]. This chapter will introduce the Aarhus STM which was used for the results presented in the thesis [18, 88].

The Aarhus STM is a homebuilt ultra-high vacuum (UHV) compatible instrument which...
2.2 The Aarhus Scanning Tunneling Microscope

Figure 2.2: Schematic illustration of the tip-sample tunnel junction during STM operation. The tip (upper part) is lowered towards the sample to a distance of \( \approx 10 \, \text{Å} \) and by applying a voltage electrons can tunnel in the vacuum junction. The ability of the STM to achieve atomic resolution is explained by a strong \( z \)-dependence of the tunnel current, whereby essentially all the current flows to or from a single atom protruding from the tip.

represents a particularly successful solution to the problem of designing a stable high-resolution microscope. It features not only state-of-the-art atomic resolution, but the compact, rigid design also allows for high sampling frequencies, i.e. quick data acquisition which enables observation of dynamic processes on the surface.

A cross-sectional sketch of the Aarhus STM is shown in Fig. 2.3(a) with an inserted sample consisting of a crystal (A) mounted on a plate of tantalum (B). Two leaf springs (C) ensure that the sample plate is held rigidly against the topplate (D) of the instrument. The cylindrical topplate is isolated both electrically and thermally by three quartz balls (E). The tip (F) is made from either poly-crystalline or single crystalline tungsten wire and electro-chemically etched to form a sharp apex. The tip is mounted on the end of the piezoelectric scanntertube (G) which provides control of the \( x-y-z \) motion of the tip during scanning of the surface. The entire scanntertube is furthermore attached to a so-called “inchworm” linear motor consisting of a SiC rod (H) which runs through another piezoelectric assembly (I) used for coarse approach of the tip to sample.

The advantage of this compact scannerhouse design is a good mechanical stability with high resonance frequencies (\( \sim 8 \, \text{kHz} \)). In Fig. 2.3(b) the entire scannerhouse (J) is mounted in the cradle, which consists of a stainless steel block (K) suspended by soft springs (O) with a resonance frequency below \( \sim 2 \, \text{Hz} \). During scanning, the entire cradle is hanging free and combined with the compact design of the STM this provides an effective screening from outside vibrations and is the only dampening needed.

The scanntertube (G) is a cylindrical tube of piezo-ceramic material (PZT-5A) which has thin silver electrodes deposited on the inside and outside. By biasing the electrodes on the piezo-ceramic tube, it can be made to lengthen or shorten on a sub-Ångström-scale and thereby provide a precise control of the \( z \) position as the tip is scanned across the surface. The lateral scanning motion is performed by bending the entire tube. The outer electrode is finely divided into four equally-sized sections running along the tube axis, as shown in Fig. 2.3(a). By applying voltages anti-symmetrically to opposite electrodes relative to the inner electrode, one side will expand while the other will contract, resulting in an overall...
Figure 2.3: Sketch of the Aarhus STM. The illustration at the top shows a cross-section of the entire STM scannerhouse (J). At the bottom, a side view of the whole STM cradle is depicted. The letters denote: (A) Crystal. (B) Sample holder. (C) Leaf springs. (D) STM top-plate. (E) Quartz ball. (F) STM tip (G) Scannertube. (H), (I) Linear inchworm drive. (K) Stainless steel block. (L) Aluminum blocks. (M) Copper braid. (N) Liquid N$_2$-cooled Cu block. (O) Suspension springs. (P), (Q) Zener diodes.
bending of the tube. Hence, the scannertube provides control of the tip position by the magnitude of the voltages applied on the \( x \) and \( y \) pairs of electrodes relative to the inner electrode.

During sample preparation, the sample (B) can be removed \textit{in situ} by pulling the sample plate out from behind the leaf springs. To prevent damage of the tip or crystal surface during this process the tip can be retracted several mm using an inchworm motor, which consists of a silver-coated piezoelectric tube with the outer electrodes divided into three cylindrical segments (I). On the inside the two outermost sections are fitted with bearings that ensure a very tight fit with the rod (H) on which the scannertube is mounted. By appropriately biasing the end sections, the tube will clamp/unclamp the rod at each end, while the middle section expands/contracts along the tube axis. By alternatingly clamping one end, unclamping the other, the elongation/contraction of the center will move the tip and scannertube towards or away from the sample – like the motion of a worm, hence the name “inchworm”. The duration of the coarse approach is roughly a minute and the motion towards the sample is terminated as soon as a tunnel current is registered.

The process of the coarse approach and scanning is fully automated and computer controlled. In the constant current mode the tunnel current \( I_t \) and tunnel bias \( V_t \) are preset by the computer controls and compared in the feedback electronics, which adjusts the tip height during scanning so that the actual tunnel current closely follows its preset value. A typical STM image consists of 256\( \times \)256 pixels, each representing information on the tip height \( z \) (or actually the \( V_z \) bias on the scannertube) and the position in the \( x-y \) plane of the surface. In this thesis the \( z \) information in STM images is represented as contour maps in a black-red-yellow color palette, where black corresponds to points with the tip close to the surface and yellow to points where the tip is further away. Alternatively, a black-gray-white scale is used for reproduction.

After the coarse approach, the tip is not always immediately in a state giving the desired degree of resolution. Typically some effort is required to treat the probe \textit{in situ} and transform the outermost apex of the tip into a favorable configuration. This can be done by gentle indentations of the tip into the surface which generally leave the tip sharper but also more unstable towards sudden changes. From experience it has been noticed that some atoms (e.g. sulfur) may favor atomic resolution better than others, and deliberately indenting the tip into such deposits (e.g. MoS\(_2\)) on the surface may yield an improved result. Additionally, the application of voltage pulses can be employed to induce field-desorption or restructuring of the outermost tip atoms which may stabilize the tip configuration and the resolution. If everything fails, the tip can as a last resort be placed about 1 \( \mu \)m away from the sample and subjected to high voltages (up to 1.2 kV), which severely changes the tip geometry. Furthermore, since the main theme of this thesis is the atomic-scale study of clusters deposited on a conducting substrate, a comment is warranted regarding the resolution of such structures with STM. To atomically resolve the edges of clusters, it is not enough that a single atom protrudes on an otherwise structure-less tip (Fig. 2.2) since this will lead to significant broadening and artificial effects near the edges. The optimum resolution is believed to occur when a microtip forms on the tip apex, i.e. a symmetric cone of atoms with a very small lateral dimension but with a length comparable to that of the cluster. In the present study, great care is taken to ensure that the tip is symmetric and only resolves real features of the structures. Generally, there is no systematic way of preparing the tip
and there is certainly no guarantees that the experiment will prevail. The success depends to some extent on the operator’s experience, luck and patience.

### 2.2.1 Variable Temperature STM

The design of the STM also allows for variable temperature operation in the range 140 K to 400 K. Temperature control of the thermally isolated top plate in connection with the sample is achieved via a heat reservoir consisting of two Al blocks (L) connected through copper-braids (M) to the top plate (Fig. 2.3). For operation below room temperature, cooling is achieved by pressing a Cu block (N) against the Al blocks while flowing liquid nitrogen through a tube in the Cu block. Once the desired temperature is reached the Cu block is removed so the cradle with the STM and Al blocks is left in free suspension. The large thermal mass of the Al blocks ensures a stable temperature throughout typical experiment durations, i.e. a typical heat leak corresponding to few degrees K per hour. Some heat is lost through the quartz balls clamping the topplate to the scannerhouse (E), thereby slightly lowering the temperature of the STM. To avoid drift problems due to this temperature change, the STM is counter-heated by dissipating power in two reversely biased 70 V Zener diodes (P). Another two Zener diodes (Q) are placed on the Al block to provide heating of the heat reservoir for STM operation at elevated temperatures. The advantage of Zener diodes compared to e.g. resistive heating, is that the necessary power is reached using small currents (and thus thin, light-weight wires) due to the large voltage drop over the reversely biased diodes. The temperature of the sample/topplate and STM is throughout the experiment monitored by means of chromel/alumel thermocouples.

### 2.3 Theory of the Scanning Tunneling Microscope

Presented with STM data, you encounter images that show contours of the surface, often depicted with a nice color palette. But what exactly is the information obtained with the STM? Intuitively, it is clear that the STM provides information on geometrical features on the nanometer scale like atomic steps, kinks and defects, but there is more to it than just this. Since we are dealing with tunneling between the tip and the surface by conduction electrons energetically near the Fermi level, it implies that the atomic details obtained with STM are somehow connected with the density of electronic states at the Fermi level, and not necessarily with the total electron density. In fact, the following theoretical description of constant current STM images shows that constant current STM images represent contours of constant local density of states (LDOS) at the Fermi level. This means that STM images often reflect a rather complicated convolution of electronic and geometric features of the surface. Although this may present some difficulties in the direct interpretation of the STM images, the additional information gained on the electronic structure of the surface in many cases turn out to reveal further and essential insight. In this section, I will briefly summarize some of the theoretical STM milestones, needed to properly deconvolute STM images and obtain new insight.
2.3 Theory of the Scanning Tunneling Microscope

2.3.1 Tersoff-Hamann Theory

The task of modelling the exact tunnel current in STM is enormous due to the inherent difficulties that lie in a description of the exact geometry of the junction (Fig. 2.2). A complete calculation of the tunneling current requires both knowledge of the electronic structure of the sample and the STM tip, which generally is in some undefined state chemically and structurally. Even if the sample and tip were both known in exact detail, the problem of modelling the tunnel junction in a complete quantum mechanical description is quite intractable in this strongly correlated system, and one must resort to descriptions with various levels of approximations.

In the perturbative “transfer Hamiltonian” approach by Bardeen [89], the tip and sample are treated as two non-interacting subsystems. Instead of trying to solve the problem for the combined system, each separate component (denoted tip (t) and sample (s) in the following) is described by their wavefunctions $\psi_t$ and $\psi_s$, respectively. The tunneling current is then calculated by considering the overlap of these in the tunnel junction. This has the advantage that for many practical systems the solutions can be found, at least approximately, by solving the stationary Schrödinger equation. For such systems the electron transfer amplitude, or the tunneling matrix element $M$, is evaluated in the model of Bardeen as

$$M = \frac{\hbar^2}{2m} \int_{S_0} (\psi_s^* \nabla \psi_t - \psi_t \nabla \psi_s^*) \, dS,$$ (2.1)

where $S_0$ is a surface lying entirely within the tunnel gap.

In first-order time-dependent perturbation theory, quantum mechanical tunneling is described by Fermi’s golden rule yielding the transition rate between two states. The total tunneling current resulting from elastic tunneling between two electrodes can thus be evaluated, for a bias voltage ($V$) applied to the tip, by summing over all states [83];

$$I_t = \frac{2\pi e}{\hbar} \int_{-\infty}^{\infty} [f(\varepsilon - ev) - f(\varepsilon)] \rho_s(\varepsilon - eV) \rho_t(\varepsilon) |M|^2 \, d\varepsilon,$$ (2.2)

where $\rho$ reflects the density of states (DOS) of the separate tip and sample systems. The electrons in both the tip and surface follow the Fermi distribution $f(\varepsilon) = [1 + \exp((\varepsilon - \varepsilon_F)/kT)]^{-1}$ and the terms take into account the exclusion principle allowing only tunneling from filled tip states into empty sample states, or vice versa. The energy shift $eV$ results from the shift of the Fermi levels by the tunneling bias. For all practical applications of STM, the temperature is low enough for the Fermi-distribution to be considered a step function, and the tunnel current can be cast in the simplified form:

$$I_t = \frac{2\pi e}{\hbar} \int_{E_F}^{E_F + eV} \rho_s(\varepsilon - eV) \rho_t(\varepsilon) |M|^2 \, d\varepsilon.$$ (2.3)

If the tunneling matrix element $M$ does not change appreciably as a function of the energy it may be separated out from the equation, and in this case, the tunnel current can be expressed as a convolution of the tip and surface DOS.

The purpose of doing STM is to learn about the surface structures, and the tip is regarded as an uninteresting probe. In this sense, it is a problem that the electronic structure...
contributes to the tunnel current according to (2.3). Tersoff and Hamann, however, extended Bardeen’s formalism and showed by simple, yet relevant approximations that the impact of the unwanted electronic structure of the tip is less pronounced at typical tunneling parameters [90, 91]. Fortunately, the Tersoff-Hamann model provides a simple conceptual framework for interpreting STM images and for that reason it is still the most widely used model.

The difficulty of evaluating the tunneling matrix element and tip electronic structure was approached by Tersoff-Hamann by assuming a simple $s$-wave tip model with wave functions centered at a point $\vec{r}_0$ in the tip. In the limit of low temperatures and low bias voltages, the total tunnel current can then be expressed as:

$$I_t \propto V \sum_s |\psi_s(\vec{r}_0)|^2 \delta(\varepsilon_s - \varepsilon_F) = V \rho_s(\varepsilon_F, \vec{r}_0),$$

in which the sum extends over sample states ($\psi_s$) evaluated at $\vec{r}_0$, and the delta function reflects that only states at the Fermi level contribute. The property on the right-hand side of equation (2.4) is a quite tractable property of the surface, the so-called local density of states (LDOS) at the Fermi level, $\rho_s(\varepsilon_F, \vec{r}_0)$, i.e. the charge density from states at the Fermi level for the bare surface evaluated at the position of the tip. Thus, the tunnel current scales to a first approximation only with this property of the surface, and low bias constant current STM images can then be considered as a reflection of contours of constant surface LDOS.

The strength of the Tersoff-Hamann theory is that it provides a simple interpretation of the tunnel current in terms of a physical quantity of the surface alone, but it also explains the exponential dependence of the tunneling bias on the tip-sample separation. All electronic states decay exponentially into the vacuum, and since $|\psi_s(r_0)|^2 \propto \exp(-2\kappa(z))$, where $\kappa$ is the decay length of the electronic states, the tunnel current will according to (2.4) have the same exponential behavior. For typical metals $\kappa \sim 1 \text{ Å}^{-1}$ and $I_t(z)$ will thus have a very strong $z$-dependence.

For metal surfaces, features of the LDOS at a distance from the surface generally coincide with the total electron density, and the contours in STM images are therefore interpreted as simple topographic maps of the surface. When adsorbates are present on the surface they alter the LDOS in the surrounding area and are in general found to be imaged as either protrusions or, counter-intuitively, as depressions with respect to the bare surface. The contrast is decided by the way the adsorbates change the LDOS at the Fermi level, i.e. if the LDOS is enhanced (depleted) the tip moves away from (closer to) the surface when scanning the affected region [92].

As a consequence one cannot always assume that maxima expected from the surface topography coincides with maxima observed in STM images. This effect becomes especially pronounced on semiconductor surfaces for several reasons. Unlike metals, semiconductors show a very strong variation of the LDOS with bias voltage. In particular, this quantity changes discontinuously at the band edges. Adding to the complexity of the contrast in STM images, the electronic structure may also be dominated by spatially localized states or dangling bonds, which generally change the picture compared to what would be expected on geometric grounds. Furthermore, one has to tunnel at bias voltages numerically larger than half the bandgap to reach empty or filled states of the sample, and the description in equation 2.4 is only strictly valid for low biases. Therefore the interpretation of such struc-
2.3 Theory of the Scanning Tunneling Microscope

The large database of STM studies, which in combination with other experimental and theoretical surface science tools have solved many problems, often rely on the Tersoff-Hamann interpretation [93–96]. In this sense, the Tersoff-Hamann theory has proved itself, but when applying it to STM studies of more and more sophisticated systems one has to be aware of the limitations. The Tersoff-Hamann approach is based on several important approximations: First of all, the tip and surface subsystems are treated independently, thus neglecting interactions as the two systems are brought into close contact. Electronically, the sample wave-functions may be distorted by the close proximity of the tip, and the forces between the tip and sample may lead to geometric relaxations of the atoms in the surface layer underneath the tip [97]. Moreover, the tip is modelled by a simple $s$-wave thus neglecting the chemical composition of the tip which may be dominated by wavefunctions with a higher angular momentum, i.e. $p$-like or $d$-like [83].

The information contained in STM images is only concerned with the electronic structure of the surface and no direct insight is gained on the chemical identity of structures. This lack of chemical specificity often makes it a difficult task to relate the observed structures of e.g. complex clusters, molecular adsorbates or reaction intermediates to their chemical nature and conformation on the surface. An interplay with complementary techniques is essential for a self-contained study. Theoretical electronic-structure calculations a commonly employed to assist STM experiments. The theoretical calculations give additional information on the possible ground state configuration of systems and furthermore can be used to generate fairly accurate simulations of STM images.

2.3.2 Simulation of STM images

One of the major advantages of the Tersoff-Hamann theory is that simulated images can be generated directly from first-principles electronic structure calculations. One such scheme of modelling the electronic structure is density functional theory (DFT), which has become a main theoretical technique employed in the elucidation of energetics, geometrical structure and electronic structure related to surfaces [98, 99]. DFT also turns out to be particularly useful in the present study and several simulated STM images will be presented to support the assignment of experimentally observed features of MoS$_2$ nanoclusters.

Density functional theory (DFT) is an efficient method to handle many-electron systems such as solids, with the only required input being the atomic number ($Z$) of the material. By iterative calculations, the atomic positions are relaxed until the minimum energy configuration is achieved, i.e. the ground state of the system. The foundation of the theory is a simple theorem [100], which states that the full many-particle ground state of an interacting inhomogeneous electron gas (e.g. a piece of solid) in a static potential is a unique functional of the electron density$^1$. Hence, all aspects of the electronic structure are completely determined by the electron density distribution in space, $n(\mathbf{r})$. Furthermore, the total energy of the system has a minimum value for a unique ground state density $n_0(\mathbf{r})$.

By self-consistently minimizing the total energy of the many-particle system of elec-

$^1$Walter Kohn was awarded the 1998 Nobel Prize in Chemistry for the development of DFT [101].
trons as a function of the total electron density, the ground state energy and density can be extracted. This is done by applying a number of tricks and approximations in which the motion of each individual electron in the solid is solved self-consistently for the density (so-called Kohn-sham equations). It is outside the scope of this thesis to elaborate on the details of a full DFT calculation, but it is worthwhile to investigate the computational setup of a typical DFT calculation in order to contemplate the limitations.

The problem of handling, in principle, an infinite number of strongly correlated electrons (a solid typically contains \(10^{24}\) electrons per \(\text{cm}^3\)) is reduced in DFT by performing calculations on periodic systems and applying Bloch’s theorem [102, 103]. When it comes to surfaces, the periodicity is broken and an additional trick has to be implemented by making use of the so-called supercells. Such supercells contain the essential structure of the surface of interest, and when repeated in all spatial dimensions it mimics a semi-infinite crystal. In this way, calculations only need to be performed in each unit cell with a limited number of electrons.

In DFT calculations involving supercells, any adsorbate or structural defect is duplicated parallel to the surface and, if insufficiently spaced, adsorbate interactions may influence the resulting structure and energy. For isolated adsorbates or defects, this artificial interaction is commonly eliminated by enlarging the unit cell until convergence is achieved in the properties of interest, e.g. an adsorption energy. The computational expense associated with such an expansion of the supercell is, however, considerable and current limitations restrict the size of the unit cell. This is important in the case of nanoclusters which ideally should each be contained in a supercell separated with enough vacuum to eliminate interactions between them. Currently, only the very first of such computationally extremely demanding studies have been presented [104–106], but as will become evident in Chapter 4 they have already, in combination with STM studies, contributed considerably to our current understanding of MoS\(_2\) nanoclusters.

In principle, DFT is an exact theory [102], but several approximations are applied in the process of handling realistic systems which leads to uncertainties in the absolute energies derived from DFT. Several schemes have been implemented in order to minimize this effect [107], but one should thus not expect a degree of precision better than 0.25 eV. However, when comparing adsorption energies for very similar systems systematic errors tend to cancel and a considerably higher accuracy can in general be achieved.

Since the output of a DFT calculation yields the electronic structure, it is furthermore fairly easy to extract the LDOS at the Fermi level of the system, and by plotting contours projected at an appropriate distance from the sample, constant current STM images are simulated. The particular contour value \(\rho_s(\varepsilon_F, \vec{r}_0)\) used to generate the STM image\(^2\) is decided by matching the measured corrugations in STM images with the corresponding calculated value. Such an approach makes no attempt to remedy the inherent approximations of the Tersoff-Hamann theory and one has to be aware that differences may exist due to tip-sample interactions. The Tersoff-Hamann theory is, however, found to be sufficiently detailed to qualitatively account for the experimental observations of MoS\(_2\) nanoclusters supported on Au(111) in this study.

For a more detailed and sometimes quantitative description of STM-images another

\(^2\)This corresponds essentially to a determination of the position of the center of tip over the surface.
class of methods have been developed, in which an attempt is made at including tip effects. These methods go beyond perturbation theory and include a proper description of the interacting sample and tip within a scattering theory formalism. One such implementation, is the electron scattering quantum chemical (ESQC) approach due to Sautet and Joachim [108, 109]3, where the tunneling process is considered to be a scattering process and the sample-tip junction is modelled by two semi-infinite bulk solids connected by a cluster of 1–15 atoms to model the tip apex. Tip effects and tip-sample interactions are thus included, and, specifically, the influence of imaging conditions like tip structure or bias voltage dependence can be systematically varied. The resulting STM simulations have in some cases allowed for quantitative structural information to be extracted from experimentally recorded images [109, 110]. The price to pay for this more elaborate simulation scheme is the large computational expense associated with modelling the tunnel junction, and for that reason less accurate electronic structure calculations are used, for example extended Hückel theory based on tight binding. Of interest in the present context is a study of the MoS$_2$(0001) surface by Altibelli et al. using the ESQC method [112]. The conclusions of this study are in qualitative accordance with those obtained obtained by the simpler Tersoff-Hamann approach in Section 4.6.

2.4 Scanning Tunnelling Spectroscopy

In this thesis, STM is used to elucidate the structure of MoS$_2$ nanoclusters deposited on Au(111). With MoS$_2$ being a semiconductor (bandgap $\sim$ 1.2 eV) and the gold support a metal, the combined system therefore represents relatively unchartered waters in terms of the usual interpretation of STM images. Furthermore, localized electronic states are frequently observed in semiconductor materials, influencing the appearance in STM images. These can be observed by mapping the whole spectrum of surface LDOS. For this purpose, another direct application of the STM is used to complement the imaging, namely Scanning Tunneling Spectroscopy (STS).

The essence of the STS technique follows from equation (2.4). If the electronic structure of the tip behaves well (i.e. constant DOS) and the matrix elements (M) is assumed to be energy independent, the conductance ($I/V$) plotted as a function of $V$ identifies directly with the spectrum of LDOS pertaining to the surface. This direct interpretation is only valid for low energies and may qualitatively be generalized in a rough, but instructive way for modest voltages by introducing a transmission coefficient, $T(\varepsilon, V)$, which is taking care of any voltage dependence and electronic structure of the tip [85]. In this way, the derivative of the tunnel current with respect to bias voltage ($dI/dV$) may be written:

$$\frac{dI}{dV} \propto \rho_s(\varepsilon - eV)T(\varepsilon, eV),$$

where $\rho_s$ is the LDOS of the sample. If the tip electronic structure is sufficiently smooth, then the $T(\varepsilon, eV)$ coefficient is a slowly varying function within a few eV on either side of the Fermi level, and features in the $dI/dV$ spectra in this interval may therefore be

3The ESQC approach has been invoked successfully in our group for both simple adsorbates (CO) [110] and large organic molecules [111].
Figure 2.4: Graph of a typical $I-V$ curve. The raw data exhibit some noise and cannot directly be differentiated to obtain $dI/dV$. The data are therefore fitted to a high-order polynomial function (full line) and from this the derivative ($dI/dV$) is computed. For all the results in this thesis, the optimum order ($n$) of the polynomial function was found to be around $n = 25$. This procedure keeps sufficiently detailed features without invoking false signals from the rapidly varying background noise of the tunnel current.

Qualitatively associated with features of the surface LDOS at or very near the surface. At best, one can say that a shape feature in the $dI/dV$ spectra is the likely result of a similar sharp feature in the surface LDOS. One cannot rule out the significance of the unknown tip electronic structure (also contained in $T(\epsilon, eV)$) which may be complicated and thus enter the $dI/dV$ signal in an unsolved manner. Conclusions in STS studies can consequently only be drawn by reproducing the spectra using a number of different tip states.

Technically, the acquisition of $dI/dV$ spectra is realized by measuring current versus voltage $I-V$ characteristics over the point of interest in the surface. The $I-V$ characteristic for each point is subsequently processed by fitting the experimental curves to a high-order polynomial function and the derivative $dI/dV$ is found (Fig. 2.4). For the subsequent analysis the $dI/dV$ signal is displayed as a function of the bias voltage, and the position of any features in the spectra may then be directly related to electronic signatures and their energetic position relative to the Fermi level. The convention for the presented data is that the tunneling bias ($V$) refers to the voltage of the sample relative to the tip, i.e. positive (negative) voltages correspond to states of the sample above (below) the Fermi level in a plot of $dI/dV$ versus $V$. It should be noted that spectroscopic data can be presented in several ways and that the normalized $(dI/dV)(V/I)$-signal sometimes gives a better quantitative agreement with the actual surface LDOS [84,86]. For the present analysis the $dI/dV$ signal is sufficient to qualitatively account for the electronic structure of the MoS$_2$ nanoclusters.

In the experimental setup, the process of STS acquisition is performed in parallel with constant current STM imaging, in order to relate the spectra directly to the surface structure underneath the tip. In each point, the tip position is frozen, the feedback loop controlling the $z$-position of the tip is momentarily interrupted and the bias voltage ($V$) is ramped in a preset interval with a simultaneous measurement of the tunneling current ($I$) to produce $I-V$ characteristics [113]. To ensure an optimum dynamic range, the frozen $z$-position of the tip is adjusted so that the maximum current does not exceed the range of the current preampli-
2.5 Remarks on STM experiments

fier (± 10 nA) nor so that it is too small to be registered on this scale. The displacement current due to the tip-sample capacitance is compensated for in the current preamplifier.

By simultaneously acquiring an STM image and STS spectra on many different points in a surface structure, changes in the $dI/dV$ spectra can be directly associated with spatial changes in the surface LDOS between preselected points in the image. Such spatially resolved STS thus circumvents one of the major disadvantages of single STS spectra, namely that the tip electronic structure is unknown and, in general, contributes in an incomprehensible way to the tunneling current. Since the tip state remains the same in different points in spatially resolved STS, the tip electronic structure represents a constant background in the $dI/dV$ curves, and changes can immediately be traced back to changes in the electronic structure of the sample.

For the spatially resolved STS of clusters, special care is taken to ensure that the STM tip is scanned in a pseudo-constant height mode between points on the cluster, i.e. the tip position is scanned at a fixed height over the cluster (but not compared to the surrounding substrate). In this way, an approximately constant tunneling matrix element is achieved and it allows direct comparison of the $dI/dV$ scans between different parts of clusters with varying conductivity (e.g. the edges relative to the basal plane). Furthermore, this operation prevents that the dynamic range of the preamplifier applied to measure the current is driven into saturation in some parts of the clusters which have a high conductivity. Constant height operation on the cluster is achieved by adjusting the gain of the feedback loop controlling tip height down to a sufficiently low value, thus effectively eliminating the response of the z-piezo and forcing the tip to follow only large corrugations, like steps or cluster edges. It was not possible to generate detailed pictures of the clusters on the Au substrate using genuine constant current mode, where the z-position of the tip is kept constant and the variation in the current are monitored as the tip traverses the surface. This may be related to the rather large differences in height of the cluster relative to the substrate.

Hence, the main direct application of STS is to study localized electronic phenomena in surfaces, and it has often been applied to do so. One should not expect anything other than a qualitative measure of the real LDOS of the surface in a rather limited voltage range, but nevertheless STS has contributed considerably to the present state of knowledge of many interesting phenomena such as electron confinement [114, 115], surface electronic states [116, 117] or the very complex electronic structure of semiconductor materials [86]. The STS technique will be utilized in Chapter 4 to monitor subtle electronic changes at the edges of MoS$_2$ nanoclusters compared to the interior of the basal plane.

2.5 Remarks on STM experiments

The very nature of the information gained in STM studies is local. This is what sets the STM and the whole family of scanning probe microscopy (SPM) techniques apart from other surface analytical techniques, viz. the ability to resolve structures and phenomena on a very small (atomic) scale. This ability is a clear advantage when one wants to study the structure of materials and phenomena on this scale, but it also leads to concerns when relating the microscopic structures under investigation to a macroscopic world. Due to the local

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4This is checked by the simultaneous acquisition of a constant current STM image.
character of the information obtained from STM images, it is not always representative of the entire system. Relying too heavily and uncritically on STM alone may lead to erroneous conclusions, a fact often referred to as “tunnel vision”. An interplay with complementary, theoretically or experimentally based surface science techniques providing crystallographic, subsurface, electronic or specific chemical information [118] is therefore essential.
Chapter 3

A Hydrotreating Model Catalyst

In this chapter the elements concerning the preparation of a novel model system for hydodesulfurization (HDS) catalysis will be described. The model system, consisting of gold-supported $\sim 30$ Å wide MoS$_2$ nanoclusters, is synthesized with starting point in the large basis of surface science knowledge on issues regarding cluster growth on metal surfaces. The present synthesis is chosen since the resulting ensemble of MoS$_2$ nanoclusters is represented by a well-characterized morphology and a narrow size-distribution. With the principal aim of studying the atomic-scale details of MoS$_2$-like nanoparticles, such a homogeneous ensemble of MoS$_2$ clusters will thus constitute a good reference for the studies.

The experimental details concerning the steps in the preparation of MoS$_2$ nanoclusters on Au(111) will be presented in the following sections. The synthesis of the HDS model can essentially be divided into two steps: First, metallic Mo is deposited onto a single crystal Au(111) substrate in an atmosphere of hydrogen sulfide (H$_2$S). In this way a template-effect of the reconstructed Au(111) is exploited to synthesize partially sulfided Mo nanoclusters with a very high degree of dispersion on the surface. Next, the clusters are crystallized into MoS$_2$ by postannealing the sample to 673 K while maintaining the H$_2$S flux.

3.1 Experimental details

The experiments were performed in a standard ultra-high vacuum (UHV) chamber with an ultimate base pressure better than $1\times10^{-10}$ mbar. Besides basic sample preparation and characterization equipment, the chamber is fitted with a home-built, high resolution STM (Chapter 2) which is the principal experimental characterization technique. The most important experimental implementations for the present work includes:

Au(111) single crystal preparation:

Prior to the experiments, a Au(111) single crystal is prepared as the model substrate. The integrity of the Au(111) “herringbone” reconstruction (Fig. 3.1) is quite sensitive towards impurities, and contaminations present in the surface are usually revealed in STM images as disruptions of the periodic pattern of the reconstruction [119]. The Au sample is cleaned by
cycles of Ar$^+$ ion sputtering (1.5 kV) and annealing (900 K, 10 minutes). This procedure generates a clean surface and a regular herringbone pattern of the Au(111) single crystal as determined by Auger Electron Spectroscopy (AES) and STM.

**E-beam deposition:**

For the deposition of metals (Mo and Co), a dedicated e-beam evaporator (Oxford Applied Research, EGCO4) is used, capable of evaporating refractory materials at sub-monolayer coverages in a controlled and reproducible manner. The evaporator features a four-pocket setup with the possibility of controlling the fluxes independently, enabling simultaneous deposition of up to four metals from separate sources. The desired evaporation rate is achieved by heating the target by electron bombardment. A stable evaporation flux is achieved by countercooling the turret containing the target rods using a built-in water cooling system. During electron bombardment of the target, some of the vaporized atoms are ionized, and by collecting this positive current (nA range) from each pocket, a relative flux measure is provided which by proper calibration can be related to the quantities deposited on the surface. Remaining ions are effectively scattered away by a high-voltage ion-retarding grid, which ensures that only neutral atoms reach the surface.

For this study, the evaporator is loaded with Mo (99.9% nominal purity) and Co (99.99% nominal purity) in the form of 2 mm rods kept in separate pockets. Upon first installation or after exposure to ambient pressures the materials are outgassed thoroughly for an extended period of time. Subsequently, the purity is checked by depositing several monolayers of material onto the Au surface and analyzing the chemical composition with Auger Electron Spectroscopy (AES). After this initial procedure, the materials only need mild outgassing at typical operating parameters of the evaporator. During evaporation only a minute increase in the background pressure of the UHV chamber to about $2 \times 10^{-10}$ mbar is registered. Calibration of the fluxes was achieved by STM measurements of the coverage. The coverages for the present study were fixed for Mo $\approx 10\%$ of a monolayer (ML) (corresponding to a flux of $\approx 1.7 \times 10^{-4}$ ML/sec, deposition time: 10 min) and for Co $\approx 2\%$ of a ML (flux $\approx 1.7 \times 10^{-4}$ ML/sec, deposition time: 2 min). Uniformity in the deposited amounts on the crystal is checked by coverage estimation from STM images of several different sections of the surface.

**H$_2$S gas doser:**

For the sulfidation, gaseous hydrogen sulfide (H$_2$S) from a lecture bottle is used (nominal purity of 99.8%) with hydrogen (H$_2$) being by far the major impurity according to the specifications. No further gas purification was done in this work. During the series of experiments different setups were used to dose H$_2$S to the chamber, which have equal performance in terms of reaching the fully sulfided state of Mo deposited on Au, but have different implications regarding the background pressure. Simply backfilling the chamber with H$_2$S to pressures reaching $1 \times 10^{-6}$ mbar was done in the first series of experiments and in experiments requiring an exact determination of the gas composition at the sample. This corresponds to a flux of approximately 0.2 ML/sec impinging on the surface, i.e. several order of magnitude higher than for the metal deposition. This rather high rate was chosen
in order to ensure sulfur-saturation of the deposited Mo. However, the repeated large exposures (up to 3500 L for a normal preparation, 1 L (langmuir) = 1×10^{-6}torr·sec) of the highly corrosive H₂S gas had unfortunate implications for the sensitive UHV equipment and pumps. Also, as a consequence of the reaction with chamber walls (and especially the Ni-coated baffle of a diffusion pump attached to the chamber), the background pressure only decreased slowly and was rarely better than 1×10^{-9} mbar.

In order to reduce the load on the equipment and improve the post-synthesis vacuum conditions, a gas doser was introduced based on the design in [120, 121]. In the doser, H₂S effuses from a reservoir through a fixed leak into the UHV environment. A transferrable stainless steel tube inside the vacuum system directs the gas directly onto the sample, thus creating a “pocket” of higher pressure surrounding the sample without the large increase in background pressures. By controlling the pressure in the gas reservoir, the effusion rate and thus the H₂S flux was adjusted. Two different methods were used to obtain a fixed leak rate from the high pressure side to the UHV side of the chamber. Either, a laser-drilled ~2 µm pinhole aperture or a simple hollow glass fibre (Ø = 75 µm inner diameter, length 2 cm) fed through a hole in a gold-coated gasket provided a stable leak rate. For each of the two geometries, the reservoir pressure was adjusted until an ensemble of fully sulfided MoS₂ nanoclusters as in the backfilling experiments was reached. This was achieved for reservoir pressures in the range ~100 torr for the pinhole aperture and ~20 torr for the glass fibre feed-through. Using the gas doser, the background is reduced to 4×10^{-8} mbar during sulfidation, and a base pressure of 3×10^{-10} mbar is reached immediately after the gas is pumped away.

The gas composition in the UHV chamber was monitored by a quadropole mass spectrometer (QMS) and during H₂S-dosing it consisted mainly of H₂S (mass 32-34) and H₂ (mass 2), with minor traces of H₂O and CO and CO₂. The relative intensity of mass 2 to 34 is approximately 1/4 or better depending on the method used to dose H₂S.

### 3.2 The model substrate

Oxidic alumina (Al₂O₃), or alternatively silica (SiO₂), supports are the preferred carriers for the industrial HDS catalysts. Because they are electrically insulating materials, they do, however, not allow for tunneling of the electrons necessary for imaging with STM, and they also present severe charging problems in electron-based spectroscopies [122]. The high bandgap of these materials thus excludes their use as substrates in model studies employing these characterization techniques. Alternatively, single-crystal graphite, which is electrically conducting, could be a candidate as a model support, not least since carbon-supported HDS catalysts also exist [29]: a single-crystalline Au(111) surface, however, holds advantages in terms of dispersion of the active catalyst material, which makes it the preferred model substrate in the present studies. Furthermore, support and adsorbate interactions are reduced since gold is noble and chemically rather inert [123].

Gold belongs to the class of metals, whose surface reconstructs in the clean state [124, 125]. Specifically, it is found that the clean surface of Au(111) is a clever choice as a catalyst model substrate, since the surface reconstructs into the characteristic “herringbone” reconstruction [126], which provides an ideal, regular array of nucleation sites for epitaxial...
The reconstruction is characterized by a \((22 \times \sqrt{3})\) unit cell in which the gold atoms in the topmost surface layer are compressed gradually by \(\sim 4.5\%\) along the [110] direction. Due to this contraction, 23 surface gold atoms are distributed among 22 bulk sites in the unit cell, resulting in alternating fcc and hcp stacking regions which run parallelly along the [112] direction. Brighter dislocation lines of Au atoms located near bridge positions are separating the fcc and hcp areas, as shown in Fig. 3.1(b). Long-range elastic interactions introduces domain boundaries, approximately every 140 Å [128]. At these boundary lines, the domains bend by alternating \(\pm 120^\circ\), and a zig-zag pattern often referred to as the “herringbone” reconstruction forms. On a length scale even larger than the image size of Fig. 3.1(a), three rotational domains appear, and thus the stress relief effectively becomes isotropic. At the domain walls, two types of elbows are observed, a pinched and a bulged elbow. The latter, which is associated with a surface dislocation, acts as the preferential nucleation site in the epitaxial growth of a number of different metals or molecules [129–131]. The surface thus provides a periodic network of nucleation sites.

In this study, the herringbone reconstruction is used as a template to disperse, in a parallel fashion, deposited metals (Mo, Co) into nanoclusters of similar size and with a well-defined nanometer separation. Figure 3.2 shows STM images of Mo deposited at a submonolayer coverage onto the Au(111) surface. Indeed, Mo is observed to belong to...
the category of metals that nucleates in a regular fashion at the herringbone elbows. The deposited Mo is seen to self-organize in equally sized \( \sim 20 \) Å wide nanoclusters dispersed onto the entire surface. For the subsequent synthesis of MoS\(_2\) nanoclusters, the high degree of dispersion and narrow particle size-distribution constitute a favorable situation since it enables direct access of gaseous H\(_2\)S and ensures a homogeneous sulfidation of the clusters during crystallization.

The actual mechanism by which metals nucleate in the herringbone elbows has been investigated previously. Only a selected range of metals have been observed to nucleate in the manner demonstrated above, here including Ni, Co, Fe, Ru, Pd and now also Mo [127, 129, 130, 132–136], whereas other metals like Cu, Ag, Al and Au do not [137, 138]. A closer look at the actual nucleation site in the herringbone elbow is demonstrated in the atomically resolved STM image of the clean Au(111) in Fig. 3.1(b). The predominant feature is the dislocation (indicated with a \( \top \) in the Fig. 3.1b) in which one Au atom has a reduced (five) and another atom an increased (seven) in-plane coordination. Whereas the brighter lines which characterize the herringbone pattern are predominantly ascribed to a geometrical shift in the surface corrugation, clearly the electronic effects also play a role at the dislocation site. The altered electronic structure localized around the surface dislocation may be prone to interact with the severely under-coordinated ad-atoms. Specifically, it is believed that a few, highly strained gold atoms near the dislocation are kicked out in an exchange process with ad-atoms. The exchanged atoms may thus form a nucleation site enabling the growth of clusters in a ripening process. The differentiation between metals that do or do not grow in this particular mode is explained by the energy gain involved in the exchange of different metal species, and by applying a model based on bulk properties by Behm et al. [130] it is found that Mo (and Co) will nucleate in the herringbone elbow, in accordance with the present STM findings.

### 3.3 Preparation of MoS\(_2\) nanoclusters

The scope of the present section is to describe the preparation which results in the most homogeneously prepared system in terms of cluster size and morphology. In order to sulfide the deposited Mo and transform it into crystalline MoS\(_2\) (Fig. 3.2), the clusters are exposed to hydrogen sulfide (H\(_2\)S). For the detailed synthesis of MoS\(_2\) nanoclusters several different procedures were tested. The parameter space associated with the preparation is vast, and to properly sulfide and crystallize the clusters into MoS\(_2\), the total Mo coverage, the H\(_2\)S exposure and the substrate temperature are important as variables.

In the procedure which will be referred to as the **standard preparation**, Mo is initially deposited for 10 min while the surface is exposed to a H\(_2\)S flux corresponding to a background pressure of \( 1 \times 10^{-6} \) mbar. Figure 3.3 shows the surface temperature during the preparation steps. Compared to pure Mo deposition (Fig. 3.2), STM images at this stage shows that the still form preferentially in the herringbone elbows, although their shape seems more irregular, i.e. the clusters appear to be in an amorphous state of sulfided Mo. In order to crystallize the clusters, the substrate is subsequently annealed to 673 K for 15 min while maintaining the flux of H\(_2\)S. After the crystallization, the sample cools to 370 K and the H\(_2\)S flux is terminated. This procedure transforms the majority of the clusters into crystalline MoS\(_2\).
Figure 3.2: STM images (4035 × 4090 Å²) of Mo deposited on the Au(111) surface at room temperature and under UHV conditions. The insert (890 × 920 Å²) shows the location of ~20 Å wide Mo nanoclusters nucleated in the bulged elbows of the herringbone reconstruction.
3.3 Preparation of MoS$_2$ nanoclusters

Figure 3.3: Illustration of the substrate temperature during the steps of the standard preparation. As the Au crystal cools down from the annealing set point at 900 K, the Mo evaporator and H$_2$S doser are prepared. At 450 K, H$_2$S is introduced to the chamber (A). The Mo deposition begins at 420 K and ends 10 min later when a coverage corresponding to 10% of a Mo monolayer is reached (B). To crystallize the sulfided metal clusters, the sample is annealed to 673 K for 15 min (C to D). The H$_2$S flux is terminated at (E) at which point the Mo has been exposed to H$_2$S for 45 min (A to E) corresponding to an exposure of approximately 3500 L (1 L (langmuir) = 1 × 10$^{-6}$ torr·sec).

Auger electron spectroscopy (AES) was used to monitor the chemical composition at different steps during the preparation. Spectra acquired of the clean Au(111) surface and the Au(111) surface exposed to H$_2$S, following the standard preparation but without Mo deposition, show no difference in neither peak intensity nor position, confirming that H$_2$S does not adsorb. Also STM images show no trace of adsorbed sulfide species on the surface. Indeed, temperature-programmed desorption (TPD) experiments show that adsorbed species desorb from Au(111) at substrate temperatures between 100 K and 160 K, i.e. well below the temperatures used in the preparation [139]. AES was also used to quantify the surface composition following the standard sulfidation of Mo. The spectrum shows distinct peaks of Mo and S, and it is concluded that H$_2$S binds to Mo. From the spectrum it is in principle also possible to quantify the ratio of S/Mo from AES, which should be close to 2 (or possibly higher for small clusters which can be super-saturated with sulfur). However, in order to obtain a substantial AES signal, the spectrum was acquired with a Mo coverage of 60% of a monolayer, and in this case the MoS$_2$ surface structures lose their well-characterized properties in terms of size and shape, which makes it a considerable task to relate the integral AES signal to cluster composition. It is noteworthy, however, that by applying a slightly modified synthesis approach, Rodriguez et al. have recently characterized MoS$_2$ structures formed on Au(111) by more sensitive synchrotron radiation...
Figure 3.4: STM image of MoS$_2$ nanoclusters synthesized on Au(111) surface following the steps of the standard preparation, i.e. the clusters were crystallized at 673 K. The size is $744 \times 721$ Å$^2$. 
photoelectron spectroscopy (XPS, UPS). By decomposing a Mo(CO)$_6$ precursor into metallic Mo clusters on the Au(111) surface and sulfiding them subsequently at temperatures up to 800 K using elemental S, photoemission spectra of the former surface structures indeed show characteristics that match very well those of MoS$_2$ [140].

Although metallic Mo deposited on Au is expected to dissolve into the subsurface region at elevated temperatures [141], the amount of Mo lost to the bulk during synthesis is found to be rather low. It is suggested that the high chemical potential of sulfur, which is maintained throughout the entire synthesis, prevents a significant fraction of the metal from dissolving into the bulk of the crystal. The total coverage of surface structures is estimated from STM images before and after the crystallization process and does not change significantly. Assuming that Mo content in the partly sulfided Mo clusters equals one layer grown pseudomorphically on unstrained Au(111), these clusters contain roughly 20% more Mo than their crystalline MoS$_2$ counterparts. It is therefore possible that this small fraction of the Mo is lost to the bulk during the high-temperature annealing. This may in turn explain why the herringbone superstructure, which was shown to act as a template for dispersing the deposited Mo, appears severely distorted in the STM image in Fig. 3.4 after the standard preparation. The disordering may be due to distortions in the delicate long-range elastic interactions responsible for the superstructure, inflicted by small amounts of Mo diffusing into the topmost layers of the Au surface at elevated temperatures. Concerning the island density, it is observed to be reduced by roughly a factor of two to $1 \times 10^{-4}$ Å$^{-2}$ from the as-deposited situation (and the island size increases correspondingly). Thus, a minor agglomeration of the dispersed islands occurs during the postannealing process.

### 3.4 Morphology

The morphology of the structures synthesized in the standard preparation is characterized by STM. The analysis of images like Fig. 3.4 reveals that the morphology of the nanoclusters is remarkably homogeneous with respect to size and shape. Of the synthesized structures the majority (> 95%) is characterized as crystalline MoS$_2$ clusters. The remaining fractions are either amorphous structures resulting from incomplete sulfidation or clusters too small to be characterized. Of the crystalline structures, the predominant shape is the triangle, which constitutes 93.7%. The remaining clusters (6.3%) also reflect the hexagonal symmetry of MoS$_2$, but have shapes of rhomboids, trapezoids, pentagons, hexagons or structures merged from these simpler geometric forms. Under the present sulfiding conditions, it is thus apparent that the single-layer triangular structure of MoS$_2$ clusters is favored. In Fig. 3.4 it is furthermore found that the orientations of the triangular structures follows the sixfold symmetry of the Au(111) surface.

The clusters are also very similar with respect to size. The cluster size distribution illustrated in Fig. 3.5 is observed to be very narrow with an average area of the triangles of $\sim 450$ Å$^2$. This corresponds to a side length of $\sim 30$ Å, which matches well the spatial extension of the active particles in typical HDS catalysts.

In conclusion, the ensemble of clusters synthesized by the standard preparation exhibits a remarkable homogeneity with respect to morphology as well as size. As a model system for the HDS catalyst, the clusters thus form a well-characterized reference for further
Figure 3.5: Size distribution for the single-layer MoS$_2$ triangles synthesized at 673 K. The mean cluster area is 450 Å$^2$, corresponding to an average side length of 30 Å in an equilateral triangle. The standard deviation is 207 Å$^2$ and the bin size is 100 Å$^2$.

experiments elucidating details on the atomic structure of the active edges, reactivity with adsorbed molecules and effect of Co promotion. The preparation described here will, consequently, be the starting point in most of the following chapters treating these important issues. The next chapter will focus on the detailed elucidation of the atomic-scale structure of the triangular MoS$_2$ nanoclusters with special emphasis on the edges which are believed to hold the active sites for hydrodesulfurization.
Chapter 4

The Atomic-scale Structure of Single-Layer MoS$_2$ Nanoclusters

In this chapter, focus will be on the determination of the detailed structure of the triangular MoS$_2$ nanoclusters synthesized in the standard preparation. The shape of a single-layer MoS$_2$ nanocluster is controlled by the two low-indexed edge terminations – the Mo edge or the S edge, see Fig. 1.6. These two types of edges are stoichiometrically different and are thus expected to enter the catalytic reaction in different ways. The question of which type of edge terminates the cluster is consequently a very important aspect.

In STM images of the triangular MoS$_2$ nanoclusters, distinct atomic-scale features of the clusters are revealed, which allows an exact structural determination of the catalytically important edges. Since both the geometric and electronic structures of the clusters are probed with STM, not only the atomic-scale geometric configuration of the edges is examined, but subtle electronic effects are also revealed, which have implications for the chemical reactivity pertaining to the edges.

4.1 Characterization

An atomically resolved STM image of an MoS$_2$ nanoclusters synthesized in the standard preparation is illustrated in Fig. 4.1. In the image, the cluster is observed to contain a plane of hexagonally arranged protrusions with an average interatomic distance of $3.15 \pm 0.05$ Å. This matches exactly the value found for the lattice on the basal plane of MoS$_2$(0001).

As described in Chapter 2, low bias, constant-current STM images reflect to a first approximation the local density of states (LDOS) at the Fermi level projected onto the position of the STM tip apex. In general, STM images thus represent a rather complicated convolution of both electronic and geometric structures on the surface. This is especially true for oxides [142, 143] or sulfides like MoS$_2$, which generally exhibit a bandgap.

In light of this, it cannot a priori be determined if the hexagonally arranged protrusions on the basal plane of MoS$_2$ reflect either the S atoms in the surface layer or Mo in the second layer (see Fig. 1.5), since the lattices of sulfur and molybdenum atoms are identical. It will,
Figure 4.1: Atomically resolved STM image ($V_t = 5.2$ mV, $I_t = 1.28$ nA) of a triangular single-layer MoS$_2$ nanoclusters on Au(111). The size of the image is $41 \times 42$ Å$^2$. 
4.1 Characterization

Figure 4.2: The apparent height of the MoS$_2$ clusters imaged at different (negative) tunneling biases. The values presented here represent average height measurements of MoS$_2$ clusters from STM images recorded at the specified bias voltages. For consistency, the data were selected from images obtained at tunneling currents in the range 0.5 nA-1.2 nA. Outside this region changes in the tunneling matrix element influences the height additionally. The fact that only negative bias voltages are shown in the graph reflects that the statistical materials was most extensive in this interval due to particularly stable tunneling.

However, be shown by means of detailed STM simulations (Section 4.6) that the lattice of protrusions on the MoS$_2$ basal plane can be attributed to the topmost layers of S atoms in the clusters in low bias STM images. This is also in accordance with previous theoretical studies on layered MoS$_2$ slabs [112, 144]. Since the hexagonal arrangement of protrusions on the basal plane of the clusters does not change in STM images by changing the tunneling parameters, the triangular-shaped islands are thus interpreted as MoS$_2$ nanocrystals with their (0001) basal plane oriented in parallel to the Au substrate and with the protrusions reflecting the hexagonally arranged S atoms in the topmost layer.

From STM line scans performed across the clusters, the cluster height and stacking is determined. As illustrated in Fig. 4.2, the cluster height exhibits a characteristic increase in the values as a function of the exact tunneling voltage, and it is seen to increase asymptotically from values below 1.0 Å at the lowest bias towards values near 3.0 Å at the highest stable tunneling conditions, which is less than the geometrical distance of 3.16 Å between S nuclei in the top and bottom S layer in a single-layer of MoS$_2$ (Fig. 1.5). This slight underestimation of the height is attributed to subtle electronic effects probed by the STM. The important issue of the electronic structure of MoS$_2$ on Au(111) will be addressed later on. The asymptotical value in Fig. 4.2, however, approaches the geometrical height of single-layer MoS$_2$, and it is therefore concluded that the clusters are present as MoS$_2$ single-layer slabs, i.e. consisting of only one of the building blocks in the unit cell of 2H-MoS$_2$. 
4.2 Morphology

The single-layer MoS$_2$ clusters synthesized in the standard preparation are observed to have a very predominant triangular morphology (Section 3.4), reflecting that this is the equilibrium shape of the MoS$_2$ crystallites under the present sulfiding conditions. From the crystal structure of MoS$_2$ (Fig. 1.6), the triangular shape of the single-layer MoS$_2$ islands directly implies that only one of the two low-indexed edge configurations is present in the equilibrated structures. As will be evident from a detailed analysis of the edge structures, all of the formed triangles are terminated by the same type of edge, which further implies that one of the two types of edge-termination must be far more stable than the other.

This can be quantified in the so-called Wulff construction: The equilibrium shape of a cluster exposing its facets will be the form which minimizes the total free energy of the entire cluster [145, 146]. For a two-dimensional (i.e. single-layer) MoS$_2$ clusters, the total edge free energy is expressed as the sum over all edge free energies times the corresponding edge length ($\sum \gamma_i \times \ell_i$). For the equilibrium shape of MoS$_2$, this condition is fulfilled by the geometrical construction displayed in Fig. 4.3. Here, the (1010) and (1010) vectors are plotted with a common origin and with a length proportional to the surface free energy of the corresponding Mo edge or S edge. The inner envelope of the tangent planes, placed at the ends of each radius vector, describes the equilibrium shape of the cluster in real space. The relative edge free energy of the Mo edge and S edge therefore determines whether the equilibrium shape is a triangle, a hexagon or a truncated shape in between. Based on these considerations, the triangular morphology implies that the ratio of the edge free energy of the S edge to Mo edge ($\gamma_S/\gamma_{Mo}$) is at least a factor of two, or vice versa, depending on which edge termination is the more stable one. It is, however, important to realize that the Wulff description is a strictly thermodynamical equilibrium description, and that the occurrence of some metastable structures like trapezoids or rhomboids indicates that some kinetic limitations are present during the synthesis (Section 3.4). Similarly, corner or other finite size effects, which become increasingly important as the clusters decrease in size, are not included in the determination of the equilibrium shape.

4.3 Edge structure

The identity of the edges which terminate the triangular MoS$_2$ clusters is addressed in atom-resolved STM images of the clusters. In Fig. 4.4 a single-layer MoS$_2$ nanocluster is displayed with a grid superimposed on the positions of the basal plane S atoms. At the edges, the protrusions are seen to be imaged out of registry with the basal plane S atoms. In fact, the protrusions are shifted half a lattice constant along the edge, but retain their interatomic distance of $\sim 3.15$ Å. This is a feature of the edges which is representative of all investigated single-layer MoS$_2$ triangles.

The question of which type of edge terminates the triangular MoS$_2$ clusters is complicated by the fact that under the sulfiding conditions of the experiment, the edges may not be simple terminations of the stoichiometric MoS$_2$, as depicted in Fig. 1.6(a). In the hypothetical bulk-truncated MoS$_2$ hexagon, S edges are terminated by a row of sulfurs positioned at bridge positions close to the bulk-terminated case, and every Mo atom retains the bulk
Figure 4.3: Illustration of the Wulff construction of a hypothetical MoS$_2$ cluster. Vectors with lengths corresponding to the edge free energies $\gamma_{Mo}$ for the (10\overline{1}0) Mo edge and $\gamma_{S}$ for the (\overline{1}010) S edge are plotted. The envelope of tangent lines drawn at the end of each vector constructs a hexagon if $\gamma_{S}$ equals $\gamma_{Mo}$. If $\gamma_{S} > 2 \times \gamma_{Mo}$ the result is a triangle (shaded cluster) terminated exclusively by the Mo edge, or vice versa for the S edge. Intermediate values result in clusters with a hexagonal symmetry and edge length ratios different from unity.
Figure 4.4: A grid superimposed on the basal plane of a triangular single-layer MoS$_2$ nanocluster. The intersections of the white lines indicate the S atomic positions on the basal plane. At the edges, the protrusions are observed to be shifted out of registry with the basal plane lattice. Illustrated to the right are STM line scans on different sections of a single-layer MoS$_2$ nanocluster. The gray arrows indicate the direction and position of the individual scans in the image: (A) across the bright brim perpendicular to the edge, (B) along the edge protrusion (C) parallel to the edge behind the brim.

coordination to six S atoms. The Mo edges, on the other hand, are terminated by a row of fourfold coordinated Mo metal ions (Fig. 4.5a), i.e. under-coordinated with respect to bulk MoS$_2$. Under sulfiding conditions, DFT calculations have shown that S will adsorb in two almost equally stable configurations [147–149], in which either one or two S atoms adsorb per Mo edge atom. In both cases the Mo atoms achieve a sixfold coordination to sulfur, like in the bulk, but as illustrated in the ball models in Fig. 4.5, significant reconstructions occur. When only one S atom is adsorbed per Mo on the edge (configuration b), the position of the S monomer is seen to be shifted relative to the bulk position, and it moves down to a bridging position in-plane with the Mo lattice. For the Mo edge with a full coverage (Fig. 4.5c) the sulfurs keep their lateral position along the edge, but in the direction perpendicular to the edge there is a tendency for the S atoms to contract and form S-S dimers [67].

Intuitively, a simple way of interpreting the edge structure in the STM image of the single-layer MoS$_2$ nanoclusters would be to assign it to the reconstructed monomer Mo edge (Fig. 4.5b), since geometrically this seems consistent with the observed shift of half a lattice constant in the STM image. However, this pure geometrical model is only valid if the protrusions at the edges directly reflect the position of S atoms and it does not account
4.3 Edge structure

Figure 4.5: Side view of ball models of the Mo edge of MoS$_2$ with different coverages (0%, 50% and 100%). (a) Mo edge exposing a row of under-coordinated Mo atoms (blue). Under sulfiding conditions, the most stable structures are saturated with S atoms (yellow) adsorbed on the edge. This occurs in two configurations which have almost equal stability, but with different total coverages of S: (b) Mo edge with S monomers, corresponding to a coverage of 50%. (c) Mo edge with S dimers, with 100% coverage. In both configurations (b) and (c), the edge Mo atoms keep the coordination to six S atoms, but structurally the edges are seen to be reconstructed compared to the bulk configuration.

for several other edge features in the STM images.

In particular, a pronounced bright brim of high electron state density is seen to extend all the way around the cluster edge adjacent to the edge protrusions (Fig. 4.1). A line scan across the cluster edge is shown in Fig. 4.4(a), and the bright brim is seen to be imaged with an intensity corresponding to an increase of $\sim 0.3 \pm 0.1$ Å above the basal plane. In atom-resolved images, this value is independent of the bias voltage. Rather than a geometrical effect, this is attributed to an electronic effect probed by the STM, reflecting subtle changes at the edges, i.e. the existence of localized electronic states at the cluster perimeter, so-called edge states. A line scan parallel to and directly on top of the bright brim reveals no systematic corrugations in this direction. This suggests that electrons are localized strongly into one-dimensional edge states perpendicular to the MoS$_2$ edges, but delocalized along the direction of the edges.

Furthermore, the STM images of the triangular MoS$_2$ nanoclusters reveal several additional effects at the edges. These effects are illustrated in Fig. 4.4 and show up as:

- A double period with an alternating bright-dark pattern is observed of the protrusions along the edge. In the STM line scan of Fig. 4.4(b) the protrusions are seen to have an alternating relative height of $\sim 0.4$ Å. Linked to this, every second protrusion appears to be more extended perpendicularly to the edge than its nearest neighbors.

- A pairwise contraction (dimerization) of S atoms located behind the bright brim is seen. The line scan in Fig. 4.4(c) of this region reveals that the S atoms are displaced laterally along the edge direction by 0.3 Å. The pairs seem to be connected somehow to the double period on the outermost edge protrusions, since they always appear on the opposite side of the bright brim relative to the lower protrusions.

Evidently, the edges have become significantly perturbed electronically and structurally compared to the simple edge termination obtained from a bulk truncation.

The electronic structure of the clusters is an interesting and important issue, since bulk MoS$_2$, consisting of infinite sheets of S-Mo-S, is semiconducting and displays an bandgap
of $\approx 1.2$ eV \cite{150,151}. The absence of electronic states available for tunneling in bulk MoS$_2$ thus implies that the clusters should be impossible to image at bias voltages numerically less than half the value of the bandgap. However, STM images of the MoS$_2$ clusters obtained by tunneling at low bias voltages ($V_t = 5.2$ mV in Fig. 4.1) are clearly possible, and this again suggests that the electronic structure of the clusters is perturbed relative to bulk MoS$_2$. In order to investigate the detailed electronic structure further, scanning tunneling spectroscopy (STS) is performed on the clusters.

### 4.4 One-dimensional edge states in MoS$_2$ nanoclusters

When a bulk material is terminated by a surface, the reduced translational symmetry perpendicular to the surface can alter the electronic structure compared to the bulk, and give rise to special electronic states that decay exponentially into the vacuum and bulk, i.e. surface states strongly localized in the surface region \cite{118}. In a two-dimensional surface layer or a cluster, electronic edge states are the one-dimensional analogues of surface states. The resulting electronic structure at the vacuum edge, whether in one or two dimensions, may be decisive for the properties of the material and play an important role for, e.g. the adsorption of gas molecules and the chemistry that takes place at the surface. Since the reactivity of the MoS$_2$ nanoclusters is intimately connected to the edges, the presence of edge states is thus of considerable interest from a catalytic point of view. In the following, data obtained with scanning tunneling spectroscopy will make it evident that such edge states exist in the MoS$_2$ triangles.

#### 4.4.1 Scanning tunneling spectroscopy on MoS$_2$

Spatially resolved Scanning Tunneling Spectroscopy (STS) combined with constant-current STM imaging on surface structures has proven to be a very powerful method to investigate localized electronic features in surfaces, such as electron confinement \cite{114,115}, standing surface electron waves \cite{116,117} or, as in this case, one-dimensional electronic states \cite{152}. Similar edge states in graphite have recently also been studied in extended graphite layers by STM \cite{153} and in hydrogen-etched pits by STS \cite{154}.

A short account of the capabilities and, equally important, limitations of the STS technique was given in Chapter 2. Here, it will suffice to mention that a measurement of the tunneling current ($I$) versus bias voltage ($V_t$) with a fixed tip-surface distance ($z$) reveals qualitative features of the electronic structure in the tunnel junction. Specifically, it has been established that peaks in the first derivative $dI/dV$ corresponds qualitatively to features in the surface LDOS, assuming a smooth distribution of states in the tip \cite{84,86}.

#### 4.4.2 Electronic structure of MoS$_2$(0001)/Au(111)

Before investigating the edges of the triangular MoS$_2$ nanoclusters on Au(111), the electronic structure of the individual components is probed in single STS scans. Figures 4.6(a) and (b) show tunneling spectroscopy ($dI/dV$) data acquired on the two separate systems,
bulk MoS$_2$(0001) and clean Au(111). All scans are averaged over points distributed over different sites in the particular surface.

The bulk MoS$_2$(0001) surface was prepared from a natural MoS$_2$ crystal (excavated in N. Korea), which was cleaved in air and mounted in the vacuum chamber. Further cleaning of the MoS$_2$(0001) surface was performed by heating the sample to 573 K in UHV for 15 minutes. This produces clean extended terraces on the surface as judged with the STM. The $dI/dV$ scans in Fig. 4.6(a) confirm the semiconducting nature of the bulk MoS$_2$, and a gap of approximately 0.8 - 1.0 eV is observed in the LDOS$^1$. Otherwise, the LDOS in the investigated region appears featureless.

The other component of the model system, the Au(111) surface, has previously been the subject of extensive investigations with STS owing to the existence of a distinct electronic surface state. In particular, this was investigated in a number of papers demonstrating standing electronic waves in the surface LDOS scattered from edges or defects in the surface layer, as a beautiful direct visualization of the quantum mechanics and wave properties of electrons [116, 117]. In agreement with these and other STS studies [114, 156, 157], an electronic feature is observed around $-0.4$ eV in the $dI/dV$ scans (Fig. 4.6b). This is attributed to the Au(111) surface state.

Separately, the two systems behave differently with respect to their conduction properties, with the Au being electrically conducting and the MoS$_2$ layers semiconducting. The question is how the electronic structure changes when the MoS$_2$ is present as nanosized crystals placed on the Au(111)? The last graph (Fig. 4.6c) shows $dI/dV$ spectroscopy data acquired exclusively on the interior (indicated with a box) of a single-layer MoS$_2$ nanocluster. For the combined system, the averaged $dI/dV$ scans reveal that the clusters have a non-zero LDOS at all tunneling biases and are thus rendered electrically conducting, in accordance with the STM findings. Furthermore, the spectroscopy data suggest that the electronic structure of the Au-supported clusters to a first approximation can be treated directly as a convolution of the two separate systems in Figs. 4.6(a) and (b). In Fig. 4.6(c), two distinct features are observed, each belonging to the separate parts of the system. First, a peak is observed at an energy corresponding to the band edge of the Au surface state, i.e. centered around $-0.4$ eV. Like all other electronic states at the surface, it decays exponentially out into the vacuum, but at a distance corresponding to the height of a single-layer of MoS$_2$ it still has enough weight to be measured with STS. Second, a pseudo-bandgap can be identified on the MoS$_2$ clusters by disregarding the peak associated with the Au surface state and extrapolating the graph. The size of the pseudo-bandgap is estimated to range from about $-1.0$ eV up to just above the Fermi level where the LDOS is still low, i.e. it is on the order of that observed for bulk MoS$_2$. Hence, it appears that the electronic structure of the clusters partly retain the semiconducting properties of bulk MoS$_2$, although the Au support donates electron density and renders it conducting throughout the whole energy range. Such a behavior is commonly observed also for otherwise insulating thin oxide films on metal supports, e.g. Al$_2$O$_3$ on NiAl(110) [158].

At positive bias values, the graph in Fig. 4.6(c) reveals some additional fine structure which can be associated with either the electronic structure of the MoS$_2$ nanocluster or states

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$^1$It is noted that this value is smaller than the value found in other studies based on e.g. photocurrent spectroscopy [150], a fact which may be related to impurities or defects present in the surface layer contributing to the conductivity. A similar size of the bandgap was found in another STS study on a natural MoS$_2$(0001) crystal [155].
Figure 4.6: Scanning tunneling spectroscopy data. Each of the three experimental curves illustrate $dI/dV$ characteristics of (a) Bulk MoS$_2$(0001), (b) Au(111), and (c) the basal plane of a Au-supported MoS$_2$ nanocluster (region inside the box in the image). In (b) and (c) the surface state of Au at $\approx -0.4$ eV is denoted by “Au ss”. The feature denoted “MoS$_2$ es” is discussed in detail in Section 4.4.3. The scans are flanked by atom-resolved STM images of the surface structure. It is noted that the images do not correspond to the actual situation and tip state during which the scans were recorded. The voltage scale is not directly comparable between the three graphs due to pinning of the Fermi level in the combined system.
4.5 Mo edges with S dimers

The energy of one of these features appears to depend consistently on the spatial position of the tip over the cluster during acquisition of the spectroscopy scans and as discussed in the following section it reflects states only existing in a spatially confined region near the edges, i.e. electronic edge states.

4.4.3 One-dimensional metallic edge states

With the aim of investigating the spatial changes in the electronic structure due to edge states in the MoS$_2$ clusters, STS spectra are acquired in a selection predefined points covering the basal plane and edge regions of a single-layer MoS$_2$ nanocluster in Fig. 4.7. Only points along the indicated line across the edge are considered. It is noted that the STM image is acquired with the tip scanning the cluster effectively in a constant height, which ensures that scans on different parts of the cluster (with different conductivities) can be compared.

The graphs displayed in the upper panel of figure 4.7 show the evolution as the $dI/dV$ scans are gradually performed closer to the edge in steps of $\sim 3\,\text{Å}$. Far away from the edges (bottom curves), a rather low intensity is found at the Fermi level due to the pseudo-gap in the electronic structure existing on the basal plane of the MoS$_2$ nanoclusters. The position of the small peak at $-0.4\,\text{eV}$ due to the surface state of Au(111) is independent of the point on the MoS$_2$ cluster, which again strongly suggests that it is an extrinsic feature.

As the edges are approached, a shift is seen in the $dI/dV$ curves at values just above the Fermi level (sequence a-g in the upper part of Fig. 4.7). Specifically, for the last three $dI/dV$ curves (e-g) acquired near the cluster edges, a peak centered around $+0.6\,\text{eV}$ on the basal plane apparently moves down in energy towards the Fermi level and, hence, into the pseudo-bandgap. This behavior is associated with the existence of one or more electronic states at the edges of the triangular MoS$_2$ nanoclusters. To obtain a direct representation of the additional electronic structure present at the cluster edges, the lower panel of Fig. 4.7(a) shows the three curves (e-g) subtracted with average STS graphs obtained on the basal plane. Here, a broad peak centered at $\sim 0.2\,\text{eV}$ above $E_F$ and extending well below the Fermi level is seen to emerge as the tip approaches the edge region. From the STM image, the edge states are seen to be localized within $\pm 3\,\text{Å}$ of the edge region and they are therefore attributed to one-dimensional electronic states at the MoS$_2$ cluster edges. Furthermore, the edge states induce a higher LDOS at the Fermi level and consequently have an outspoken metallic character. The spectroscopy data thus confirm that the bright brim found in the atom-resolved STM image (Fig. 4.1) is the result of one-dimensional electronic edge states.

4.5 Mo edges with S dimers

The properties of the electronic edge states may have a decisive influence on both the geometric and electronic structure, and, hence the imaging of the edge structure in STM images. To investigate how this possibly influences the naïve assignment of the edge structure based on geometric grounds (i.e. that the Mo edges are terminated with S monomers), DFT calculations are performed to assist the STM studies. A comparison of the edge signatures observed with STM and input from DFT calculations and STM simulations then allows an unambiguous determination of the electronic and geometric edge structure of the triangular
The Atomic-scale Structure of Single-Layer MoS$_2$ Nanoclusters

Figure 4.7: Spatially resolved scanning tunneling spectroscopy on a triangular single-layer MoS$_2$ nanocluster. The STM image (right) was scanned with the loop gain set at a sufficiently low value to ensure an approximate constant tip height over the cluster during acquisition of the spectroscopy data. The upper panel of the graph shows $dI/dV$ curves obtained on the different points of the cluster. The points are labelled with the letters (a-g), and are each separated by $\sim 3$ Å. The baseline of the curves is offset with a fixed value to show more clearly the gradual change as the cluster edge is approached. Au ss denotes the surface state of Au(111) and MoS$_2$ es denotes an edge state. The lower panel shows the scan subtracted by an appropriate average of the basal plane.

single-layer MoS$_2$ nanoclusters. The theoretical work was performed by Mikkel Bollinger at the Technical University of Denmark [159].

The calculations are performed on an unsupported semi-infinite slab of MoS$_2$ exposing both the S edge and Mo edge simultaneously (see Fig. 4.8a). The model system consists of a stripe of MoS$_2$ repeated in a supercell geometry and with each layer separated by a sufficient vacuum distance to reduce interaction between neighboring layers and edges. The width of the unit-cell (shown with the cage in Fig. 4.8a) is adjusted to account for interaction along the edges, and a width of 1 or 2 Mo atoms is generally found to be sufficient. Similar computational setups are used in Chapters 5, 6 and 7. For reference, a short outline of the capabilities and, equally important, the limitations of DFT is given in Chapter 2.

The size of the unit cell in present study is chosen large enough for the calculations of the band structure on the basal plane (i.e. without interference from the edges) to reproduce the semiconducting characteristics of MoS$_2$. A calculated value for the bandgap of 1.64 eV is found. For reference, the calculated band structure of an infinite MoS$_2$ layer is also
Figure 4.8: (a) Unit cell used for DFT calculations of single-layer MoS$_2$. (b) Energy bands associated with the MoS$_2$ slab exposing the S edge and the Mo edge (red lines) and the corresponding plots for an infinite MoS$_2$ layer of the same size (green lines). The bandgap of the infinite layer is clearly outlined. For the edge-terminated system, three edge states are identified associated with the bands crossing the Fermi level. (c) Illustration of the contours of the electronic wavefunctions associated with edge states I and II localized entirely at the Mo edge.

displayed with green lines in Fig. 4.8(b).

The electronic structure near the edges is indeed seen to be significantly perturbed relative to the bulk. In Fig. 4.8(b), the band structure (red lines) is shown for an MoS$_2$ slab terminated by the fully saturated S edge and the Mo edge covered with S dimers (Fig. 4.5c). It is seen that three bands protrude into the semiconducting gap of MoS$_2$ and cross the Fermi level. This implies the existence of three electronic edge states with metallic properties, labelled I, II, and III, respectively. A direct inspection of the corresponding Kohn-Sham wavefunctions (Fig. 4.8b) reveals that the metallic edge states I and II are localized entirely on the Mo edge with S dimers, whereas edge state III is associated with the fully covered S edge (not shown).

Edge state I has a Fermi wave vector of $k_F \approx 0.39$ Å$^{-1}$, and is seen to be almost completely localized at the S dimers (Fig. 4.8c); it is a superposition of $p_x$ orbitals extending in two parallel chains along the edge. Edge state II is seen to extend over the first three rows having $k_F \approx 0.67$ Å$^{-1}$. The nature of this state is somewhat more complicated than for I. It is primarily constituted by two bonds: (i) the $d$-$d$ bond between the first row of Mo atoms and (ii) the $p$-$d$ bond between the second row of S atoms and the Mo atom behind.

The question of whether the metallic edge states are responsible for the striking bright brim in the STM images or not is revealed by STM simulations based on the Tersoff-
Figure 4.9: Simulated STM images of the Mo edge with S dimers without (a) and with (b) Au(111) substrate effects included. The positions of the individual atoms are represented with atom balls (small: S, big: Mo). For clarity the atoms of the Au layer are not displayed in (b). The calculated STM images follows contours of constant LDOS corresponding to $\rho(r_0, E_F) = 8.3 \times 10^{-6}$ electrons/eVÅ$^3$. This value is determined by matching the experimental corrugation measured along the close packed row of S atoms in the interior of a nanocrystal to the corrugation of the simulated images. For reference see Section 4.6.

On geometric grounds, the half-saturated Mo edge with monomers was suggested in Section 4.3 to be a possible edge termination of the triangular clusters. This edge termination is, however, found to be semiconducting implying that protrusions at the edges are not imaged at all. Since this type of edge would then be imaged significantly differently than...
observed with STM, it can be excluded. For the other fundamental type of edge termination, the S edge, metallic edge states are also found to be present, but they do not change the simple geometric interpretation of protrusions reflecting the positions of S atoms at the edges, which are in registry with the basal plane, and the S edge can thus also be excluded. The half-saturated Mo edge and the S edge will be the subject of Chapter 7, since they will be exposed under more reducing conditions and a detailed discussion of their structure is therefore deferred. Under the sulfiding conditions in the experiment, it is concluded that triangular single-layer MoS$_2$ nanoclusters are terminated with the Mo edge covered with S dimers.

### 4.6 Influence of Au(111)

Although the agreement between experimental STM images and theoretical modelling of the edges performed on an unsupported MoS$_2$ slab proves to be excellent, the question naturally arises to which extent the Au(111) substrate influences the MoS$_2$ nanoclusters structurally, electronically and in particular with respect to the electronic edge states. Clearly, the Au support must have some effect on the cluster properties since it is possible to image the interior of the MoS$_2$ clusters at bias voltages numerically less than half the bandgap of MoS$_2$.

From the STS data (Fig. 4.6), it was seen that the electronic structure of the MoS$_2$ basal plane to a first approximation can be described as a superposition of the two constituents, the Au(111) and the semiconducting MoS$_2$(0001). In this way, the basal plane of the MoS$_2$ nanoclusters is rendered metallic at all bias voltages. In particular, a surface state pertaining to the Au is observed at energies situated inside the bandgap of MoS$_2$. However, at all tunneling parameters the MoS$_2$ clusters exhibit the hexagonal arrangement and interatomic distance of the MoS$_2$ basal plane (3.15 Å) and not that of Au(111), which has an interatomic distance of $\approx 2.8$ Å in the topmost layer. Therefore, the STM results imply that the electronic states of MoS$_2$ and Au mix to some degree, so that the MoS$_2$ lattice is reflected in STM images.

In order to investigate this, the effect of the Au support on the electronic structure of MoS$_2$ was included in the (DFT) calculations (see also Ref. [104]). The calculational unit cell was extended by adsorbing an MoS$_2$ slab on top of a pseudomorph, two atomic-layer thick Au(111) substrate assuming epitaxial growth. Both an infinite MoS$_2$ slab and a stripe geometry similar to that in Fig. 4.8 were modelled in the DFT study to investigate the effect of Au on the MoS$_2$(0001) basal plane and the edges, respectively.

For the infinite MoS$_2$ slab, the calculations show that Au(111) interacts weakly with the MoS$_2$ layer and it does not significantly change the geometric structure of MoS$_2$, verifying the inertness of the Au as a model substrate. Electronically, however, the Au substrate induces a change on the basal plane of MoS$_2$, where in principle no states are available at the Fermi level. This is illustrated in Fig. 4.10(a), where electronic energy bands of MoS$_2$/Au(111) are selected and shown along with bands of isolated MoS$_2$ and Au(111). Although the unit cell was too small to develop the Au(111) surface state, it is seen from the dispersion curves that the valence band of MoS$_2$ interacts with one of the metallic Au conduction bands. Near the center of the Brillouin zone a large splitting of the valence and
Figure 4.10: Calculation of an infinite layer of MoS$_2$ on Au(111). MoS$_2$ is placed on a pseudomorph Au layer consisting of two atomic layers (lattice constant 3.16 Å) and the resulting band structure is calculated. (a) Comparison of selected energy bands (red) of a MoS$_2$/Au(111) layer with the corresponding energy bands of the MoS$_2$ slab (green, dashed) and the Au(111) surface (blue, dotted) separately. (b) Simulated STM image of a $1 \times 1$ unit cell of MoS$_2$(0001) on Au(111). The large and small balls superimposed on the image illustrate the positions of Mo and S, respectively. For clarity the positions of the Au atoms are omitted. (c) The calculated STM image follows contours of constant LDOS corresponding to $\rho(r_0, E_F) = 8.3 \times 10^{-6}$ electrons/eVÅ$^3$. At this value, the corrugation along the close-packed direction on the S lattice matches the experimental value ($\sim 0.22$ Å). The graph shows line scans of the experimental (full) and simulated corrugation (dotted) on the basal plane of MoS$_2$(0001) on Au(111).

Conduction band of the combined MoS$_2$/Au system is found. Further out in the Brillouin zone the shape of the combined bands primarily identifies with either the unperturbed MoS$_2$ valence band or the Au band, respectively. The interaction of the MoS$_2$ slab and the Au surface is seen to result in an avoided crossing between the Au conduction band and the MoS$_2$ valence band. This has important implications for the electronic structure at the Fermi level for the combined system. The states passing the Fermi level are dominated by the Au state, but they will also have a small weight on the MoS$_2$ valence band, i.e. the gold substrate lifts the MoS$_2$ states up to the Fermi level.

A simulated STM image of the (0001) basal plane of MoS$_2$/Au(111) is shown in Fig. 4.10(b). The image was generated by means of the Tersoff-Hamann scheme and based on DFT calculations of the system outlined above. The image is simulated from the LDOS at the Fermi level for the combined system, and the protrusions on the basal plane of MoS$_2$ are confirmed to reflect the position of the S atoms for the Au-supported MoS$_2$ clusters. The clusters are therefore concluded to partly loose their semiconducting properties as a result of the electronic interaction with the Au substrate, and it is found that protrusions on the basal plane of the cluster reflect the positions of the S atoms in the STM images, even for bias voltages inside the bulk MoS$_2$ bandgap.
This connection may also qualitatively explain the bias dependence of the apparent height of the clusters. In Fig. 4.2 the cluster height is measured on the basal plane relative to the Au substrate and is seen to increase asymptotically from rather low values at bias voltages near the Fermi level to values which match that of single-layer MoS$_2$ at bias voltages well outside the pseudo-bandgap, i.e. at values exceeding $-1.0$ V. The low apparent height of the single-layer clusters results from the fact that tunneling inside the pseudo-bandgap is governed by the mixed electronic structure of MoS$_2$ and Au, the LDOS of which, when it is projected onto the tip apex, has a low weight. As the bias voltage is gradually increased, more states become available for tunneling due to the integration of the state density, effectively increasing the cluster height. At bias voltages well outside the bandgap, the electronic structure is dominated by MoS$_2$ and height becomes more reminiscent of the geometrical cluster height.

With respect to the one-dimensional edge states, neither the appearance of the bright brim nor the shifted geometry of the outermost protrusion are seen to have a significant dependence on the tunneling conditions in STM images. The height of the brim relative to the basal plane is measured to be $\sim 0.3 \pm 0.1$ Å in atom-resolved images in a large interval of bias voltages. This immediately suggests that the electronic structure associated with the one-dimensional edge states in the MoS$_2$ triangles is only weakly affected by the Au substrate, and their electronic structure in STM images can thus be treated as a constant contribution to an otherwise bias-dependent background.

DFT calculations that include the effect of the Au substrate on the MoS$_2$ edges confirm this picture. A simulated STM image of an MoS$_2$ slab adsorbed on a Au(111) substrate is illustrated in Fig. 4.9(b) exposing a section of the Mo edge with S dimers. In the simulated image, the edge retains the bright brim, and the outermost protrusions are still seen to reflect the interstitial space between S dimers, i.e. the features associated with the metallic edge states are only weakly affected by the Au. As expected from the calculation on the infinite basal plane of MoS$_2$ on Au, the interior of the cluster becomes slightly conducting and is thus imaged with protrusions reflecting the position of S atoms, all in accordance with the STM findings. In conclusion, the Au is seen to affect the electronic structure on the basal plane of the single-layer MoS$_2$ nanoclusters, whereas the electronic edge states appear to be affected only weakly.

As a model system for the active particles in HDS catalysis, the results of this section are important since they demonstrate that the edges, which are believed to be the only catalytically active part of the clusters, are left essentially unaffected by the gold substrate, both geometrically and electronically.

### 4.7 Finite size effects in MoS$_2$ nanoclusters

The double period exhibited by the outermost edge protrusions and the apparent pairing in the row behind the bright brim observed in the atom-resolved images of the single-layer MoS$_2$ triangles (Figs. 4.4b,c) do not find an immediate explanation in terms of the electronic edge states. This rises the question whether corners could be responsible for additional atomic relaxations along the edges or electronic fine-structure perturbations resulting from quantum size confinement in the small clusters. Due to the semi-infinite geometry of the
MoS$_2$ slab, the DFT calculations presented in the last section cannot address the influence of corner or finite size effects, and are consequently not sufficient for a total description of the MoS$_2$ nanoclusters.

Very recently, cluster DFT calculation have been performed in order to shed light on the cluster properties and the effect of corners [104, 105]. Preliminary results reveal that the experimentally observed double period can be explained by a slight structural rearrangement of the S dimers of the Mo edge-terminated MoS$_2$ cluster. In the calculations, the S dimers are found to have a tendency to pair up along the lateral direction of the edge (see Fig. 4.11), and in STM simulations this restructuring of the edge clearly leads to a similar variation in the intensity of the edge protrusions [104, 105]. This effect originates from the characteristics of edge state $I$ (Fig. 4.8c), which is a superposition of $p_x$ orbitals along the S dimers of the Mo edge. When the lateral distance between each pair of S dimers is changed due to the formation of pairs, the overlap between the $p_x$ orbitals is decreased (increased) and a corresponding reduction (enhancement) in the electron density between the S dimers thus results in the observed pattern with a periodicity of two lattice constants along the edge protrusions. Since the pairing effect only occurs in clusters and not in infinite slab calculations, the energetic stabilization of the pairs must be a result of the finite size of the edges or the presence of corners. The pairing of S atoms behind the brim observed with STM (Fig. 4.11) finds no immediate explanation, but since it appears with the same regular pattern in STM images as the double period, a coupling of edge state $I$ is suggested to exist to the atomic rows behind. All the additional edge features may thus be traced back to the formation of dimer pairs along the edge.

The possibility of S dimers forming pairs along the edges is furthermore found to have a profound influence on the equilibrium morphology of the MoS$_2$ nanoclusters, since all of the triangular MoS$_2$ clusters imaged in atom-resolved STM images are (i) found to exhibit the double period and (ii) exclusively terminated by an odd number of edge protrusions. Since protrusions reflect the interstitial space, the STM results thus show that the cluster edges always contain an even number of S dimers. For instance, the MoS$_2$ cluster shown in Fig. 4.1 exhibits 11 edge protrusion, corresponding to 12 dimers. This apparent quantization of the number of edge S dimers is surprising, since the crystal structure of MoS$_2$ does not restrict this number. Interestingly, in cluster calculations by Schweiger et al. [105], the double period pattern is found to be dependent on the parity of the edge, i.e. it is only
energetically favorable when the number of edge dimers is even like in Fig. 4.1. This piece
of information may explain the observed stability of MoS\textsubscript{2} clusters terminated exclusively
with even numbers of dimers in the STM images. The preference for the cluster to assemble
with edges counting only an even number of dimers is interpreted in terms of frustration
effects occurring at the cluster corners. If an odd number of dimers is present, one terminal
S dimer cannot be paired, thus leading to a less stable situation. The pairing of S dimers and
the occurrence of magic numbers on the edge lengths are thus intimately interrelated, and
the observed stability of quantized edge numbers represents direct experimental evidence of
finite size effects influencing cluster morphology of MoS\textsubscript{2}.

Energetically, the stabilization effect associated with the formation of an even number
of dimer pairs seems extraordinarily pronounced, since only a very few clusters with defects
(i.e. due to edge kinks or truncated shapes, Chapter 8) are found to deviate from this rule.
Some clusters may be forced into a truncated shape by a defect and hereby to exhibit an
edge with an even number of protrusions, and accordingly, such edges do not exhibit the
double period. It is, however, stressed that this does not occur for the triangular-shaped
MoS\textsubscript{2} nanoclusters, strongly suggesting that a large energy is gained by assembling with
even numbers of S dimers.

A simple estimate of the relative stability can be achieved by using Boltzmann statistics
[160], in which the probability of having an edge which is not allowed to form dimers
\(P\text{_{odd}}\) is compared to an edge which is allowed to do so \(P\text{_{even}}\). In the hypothetical absence
of any energy contribution associated with the pair formation, the two situations where
clusters are terminated with an even or odd number of dimers should, in principle, be equally
stable. Treating these two situations in terms of their population \(N\text{_{odd}}\) and \(N\text{_{even}}\), the extra
energy gained by forming dimers will shift their numbers correspondingly, and the size of
the contribution can be estimated as:

\[
\frac{N\text{_{odd}}}{N\text{_{even}}} = \exp\left(\frac{\Delta E_{\text{pair}}}{k_B T}\right),
\]

The \(\Delta E_{\text{pair}}\) can thus be considered as the additional energy gain (cost) associated with the
situation where the triangular cluster grows another shell, i.e. from an even to an odd number
of dimers or vice versa.

From the present ensemble of more than 100 atom-resolved images of edges in regular
triangular-shaped MoS\textsubscript{2} clusters, all were found to exhibit the double period and conse-
quently an even number of S dimers. With a probability of having a cluster terminated
without the double period \(N\text{_{odd}}/N\text{_{even}}\) of less than 1/100 (and possibly much lower), this
translates from equation 4.1 to an energy difference \(\Delta E_{\text{pair}}\) of at least 0.25 eV between the
two situations at the synthesis temperature (673 K), i.e. a significant extra stabilization. This
energy is most likely even higher, but without the possibility of extracting the exact lower
limit of \(P\text{_{odd}}\) a deeper statistical treatment is beyond the scope of this thesis. Since the en-
tire edge reconstructs, \(\Delta E_{\text{pair}}\) should be considered as a collective property of the S dimer
terminated edges as a unity, and the interaction with the corners can thus be considered to
be of relatively long range.

The stabilization of magic edge lengths may, in turn, also explain the outspoken homog-
geney of the cluster shape and size. Since the amount of sulfur contained at the edges is
quantized, this also means that the amount of Mo in each cluster must be constrained during
growth. Remarkably, the effect appears to be so strong that it only allows the clusters to
grow in quantized sizes during synthesis (i.e. in shells with 6, 8 or 10 edge S dimers, etc.).
In this way the actual size of the clusters becomes quantized. One can imagine a growth
scenario in which the MoS$_2$ islands nucleate and only grow if the impinging amount of ma-
terial (diffusing on the surface) is high enough to create another stable shell. Conceptually,
this growth mode is thus considerably different from normal nucleation and growth of is-
lands, where cluster size is determined by the given amount of material within the capture
zone of the islands [161]. On top of the regular limitations present due to the limited amount
of Mo available locally, the requirements for the cluster to assemble in shells become more
and more difficult to fulfill for the larger cluster, and this may explain the rather narrow size
distribution in Fig. 3.5 and the extraordinary homogeneity of the triangular shape.

Since finite size effects play a role in the stabilization of the triangular shape, the simple
Wulff construction reported in Section 4.2 breaks down, and a more elaborate model is
needed in order to extract the exact ratio of edge free energies ($\gamma_{\text{Mo}}/\gamma_{\text{S}}$). The energy
contribution due to corners can be included in the description of the free energy for the
small clusters, but since the observed effects are not only associated with the corners but
rather a collective effect of the entire edge this is very difficult. As a qualitative argument
the predominance of the triangular shape under the present sulfiding conditions may instead
be explained by the additional energy gained by an even amount of S dimers forming pairs
on the Mo edge. If a similar mechanism does not exist for the opposite S edges, the balance
between the edge free energies ($\gamma_{\text{S}}/\gamma_{\text{Mo}}$) will in an equilibrium description certainly be
tipped further in favor of the Mo edges.

The existence of finite size effects providing an extra energy gain of the paired S dimers
may also explain the experimental findings that only S dimers are observed, although semi-
infinite DFT calculations predict the monomers to be of equal stability [67, 104, 148]. A
further stabilization of the Mo edge due to S dimer pair formation in finite clusters will of
course favor the full 100% coverage, if a similar effect does not exist for the S monomers
on the Mo edge. In light of the impact evidenced by the above considerations, the energy
associated with the pair formation is speculated to be considerably higher than the lower
limit of 0.25 eV extracted from the simple statistical treatment, maybe of the order of several
eV for each edge.

In conclusion, finite size effects associated with corners seem to impact profoundly both
the shape and edge geometry of the MoS$_2$ nanoclusters under sulfiding conditions. This has
direct implications for the stability of the S atoms at the edges, and as will be shown in the
next chapter it influences the tendency to form the S vacancies, believed to be active sites
for HDS.

4.8 Conclusions on triangular single-layer MoS$_2$ nanoclus-
ters

It is found on the basis of atom-resolved STM images and STS data combined with input
from DFT that the single-layer triangular MoS$_2$ nanoclusters synthesized in the standard
preparation are terminated by the Mo edge covered with S dimers. Intuitively, this is also
expected since the clusters are synthesized under a large chemical potential of S, driving the
Figure 4.12: The evolution of shape and size of single-layer MoS$_2$ nanoclusters as a function of postannealing temperature. For all experiments the annealing period was fixed at 15 minutes. The standard preparation is at 673 K (a) Shape analysis of the clusters resulting from different preparations. The fractions in the block diagram are indicated as: triangles (black), non-equilibrium structures (dark gray) and different structures with hexagonal symmetry (light gray). (b) Mean size of the single-layer MoS$_2$ cluster plotted versus postannealing temperature. The error bars show the standard deviation of the size distribution.

coverage on the edges towards full saturation. Compared to a simple description derived from bulk properties of MoS$_2$, it is found that the cluster edges are considerably reconstructed, both structurally and electronically. The existence of one-dimensional metallic edge states of the MoS$_2$ cluster was inferred from STS and DFT studies. The STM images furthermore reveal a range of additional edge features ascribed to finite size effects. All of the above features are indeed found to be inherent to the cluster and not the gold support and may thus have decisive influence on the chemical reactivity of the edges with respect to HDS. A detailed investigation of the adsorption and reaction properties of the cluster edges is the subject of the next chapters. Before entering this important subject, it is worthwhile to discuss some other properties of the structures formed in the preparation of MoS$_2$ on Au(111).

4.9 MoS$_2$ morphology by variations in the preparation parameters

The parameters of the standard preparation are chosen for the synthesis, since these results in an ensemble of clusters which is well-characterized with respect to morphology and size. This optimum preparation was found by a series of experiments where the phase space of different preparation parameters was investigated, especially by varying the substrate temperature during postannealing and the annealing duration.

Substrate temperatures of at least 673 K are required during the postannealing step in order to crystallize the MoS$_2$ clusters properly. A further increase in temperature is seen to affect both the size distribution and morphology of the surface structures. Based on large-scale STM images the morphology of the single-layer MoS$_2$ nanoclusters was monitored in terms of cluster shape and size, and the effect of a higher substrate temperature during
postanneling (673 K - 873 K) is summarized in Fig. 4.12.

As a consequence of the increase in postannealing temperature, a large mobility of the surface species is activated leading to a pronounced agglomeration. In the Fig. 4.12(a) this is evidenced by an increase in the average size of the single-layer MoS$_2$ slabs combined with a significant broadening of the size distribution. Furthermore at the highest temperatures, the coverage of single-layer MoS$_2$ on the terraces of the Au(111) substrate decreases, and larger single-layer MoS$_2$ platelets start to form near the step edges on the gold substrate, as illustrated in Fig. 4.13(a). It should be added that only the single-layer MoS$_2$ clusters far from step edges contribute to Fig. 4.12, and that the total coverage of single-layer slabs stays constant in the different preparations. Apparently, the gold substrate loses its ability to locally confine the material. The agglomeration probably occurs by cluster diffusion or a ripening process where evaporation and subsequent surface diffusion of metal atoms or sulfur-metal complexes occurs, followed by recapturing by other islands either on the terraces or near step edges.

The agglomeration into larger clusters explains why the shapes of the MoS$_2$ nanostructures appears less homogeneous at higher temperatures as shown in Fig. 4.12(b). In the graph the fraction of metastable MoS$_2$ structures shaped as trapezoids, rhombs, pentagons or hexagons or other structures merged from these increases at the expense of the triangular structures, proposed to be the equilibrium shape. Apparently, perimeter diffusion on the larger clusters is too slow for the clusters to reach the thermodynamically stable triangular form during the time of the experiments. Also the impact of finite size effects, which to some degree determines the triangular equilibrium shape, will be diminished for the larger clusters. This tendency, which is most pronounced as the substrate temperature is increased beyond 773 K, is, however, reversed by increasing the annealing duration from the default 15 min. For instance, annealing the surface at 823 K for 30 min while keeping the H$_2$S background, results in an increase in the fraction of triangles from 15% to 25%, without any significant increase in the mean size of the clusters. Hence, it can be concluded that the triangle is the equilibrium form of the single-layer MoS$_2$ clusters under the sulfiding
4.10 Stacked MoS$_2$ nanoclusters

By far the majority of the clusters synthesized in the standard preparation (Fig. 3.4) are concluded to be present as single-layer MoS$_2$ slabs, but around 1% of the clusters are found to be imaged significantly higher (> 4.5 Å in Fig. 4.14). These clusters are also considerably

**Figure 4.14:** STM image ($V_t = -1973$ mV) of a two-layer MoS$_2$ cluster synthesized in the standard preparation at 673 K. The stacked clusters are easily recognized by their large size and brighter appearance compared to the single-layer structures. The line scan indicates the difference in height of a single-layer and a two-layer MoS$_2$ nanocrystal.

conditions of the experiment.

The large MoS$_2$ platelets grown by step flow growth at the Au terraces reveal information on the hetero-epitaxial growth of MoS$_2$ crystallites on Au(111) (Fig. 4.13(b) and (c)). On the large single-layer MoS$_2$ islands a distinct hexagonal superstructure is clearly visible on the basal plane with a periodicity of $\sim 34$ Å and a corrugation of $\sim 0.4$ Å along the closed-packed directions. This is accounted for as a Moiré overlayer pattern resulting from the hetero-epitaxial growth of the MoS$_2$ on the Au(111) substrate. In atom-resolved STM images the closed packed directions on the basal plane of the MoS$_2$ clusters and the Au(111) are found to coincide. In such a non-rotated, hexagonal overlayer (with a lattice constant $a_o$) on a hexagonal substrate (with lattice constant $a_s$), atoms in the overlayer will reside alternatingly on on-top sites and high-coordination sites on the substrate. Consequently, the incommensurate overlayer will exhibit a superstructure with a periodicity of $a_s \times a_o / (a_o - a_s)$ [162, 163]. Assuming an unreconstructed Au(111) lattice constant of $a_s = 2.88$ Å and using the observed lattice constant of MoS$_2$ $a_o = 3.15$ Å, the calculated beating frequency is 33.6 Å, in agreement with the STM findings. A close inspection of the smaller atom-resolved MoS$_2$ nanoclusters also reveals signatures of this Moiré pattern, exemplified e.g. in Fig. 4.1 as the small level differences along the edge, and the hetero-epitaxy between MoS$_2$ and Au(111) thus appears to apply in both the small structures and the extended layers. The Moiré superstructure is most likely a structural effect resulting from the fact that the MoS$_2$ clusters are laterally stiff (the lattice constant is preserved) but vertically flexible. Indeed, this flexibility of MoS$_2$ layers is well known from other studies [164] and is especially a hot topic in relation to the formation of MoS$_2$ nanotubes and other fullerene-like structures [165, 166].

4.10 Stacked MoS$_2$ nanoclusters

By far the majority of the clusters synthesized in the standard preparation (Fig. 3.4) are concluded to be present as single-layer MoS$_2$ slabs, but around 1% of the clusters are found to be imaged significantly higher (> 4.5 Å in Fig. 4.14). These clusters are also considerably
bigger (area \(> 1000 \text{ Å}^2\)). From atom-resolved STM images it is revealed that these structures have exactly the same hexagonal lattice as the single-layer clusters, and they are therefore interpreted as two-layer high MoS\(_2\) clusters. The geometrical height of a two-layer MoS\(_2\) slab is 9.3 Å (Fig. 1.5). The considerably smaller height observed for the two-layer slabs is again primarily attributed to the perturbed electronic structure of MoS\(_2\) on gold.

With respect to morphology, the higher clusters are found to adopt a triangular shape. This is surprising, since in the bulk 2H-MoS\(_2\) stacking of MoS\(_2\), alternate layers will expose Mo edge and S edges, successively (Fig. 1.5), and in equilibrium, multilayer clusters are thus expected to grow in a perfect hexagonal form only, since the difference in edge energies tend to cancel. The existence of predominantly triangular-shaped two-layer islands, thus implies that the clusters do not follow the 2H-MoS\(_2\) bulk stacking frequency of MoS\(_2\) (Fig. 1.5b).

One can speculate on the reasons for this surprising fact: It is suggested that the interlayer interactions controlling the separation between the layers are significantly different in the two-layer clusters compared to the weak van der Waals forces separating layers in bulk 2H-MoS\(_2\). This may be due to additional attractive interactions at the edges causing the clusters to follow the triangular shape of the bottom S-Mo-S layer and possibly also reduce the geometric interlayer distance. In atom-resolved STM images of the two-layer triangles, the edges are found the display the same structure as the single-layer MoS\(_2\), i.e. terminated by the Mo edge with S dimers. The fact that both the bright brim and shifted position of edge protrusions is retained in the topmost layer of MoS\(_2\) again underlines that the metallic one-dimensional edge states are inherent to MoS\(_2\) and not the Au support.

Interestingly, the morphology of the two-layer MoS\(_2\) slabs evolves in a different way than for the single-layer clusters when the synthesis temperature is raised. Unlike the single-layer counterparts, the coverage of the stacked islands present on the Au terraces does not decrease when the postannealing temperature increases, simply reflecting that the two-layer structures somehow have a smaller mobility and keep their position on the basal plane, whereas single-layer islands possibly break up and diffuse towards step edges. The clusters are, however, seen to transform from the large triangles (see Fig. 4.14) found at 673 K into even larger predominantly hexagon-shaped structures. Two of these are seen in Fig. 4.15. It appears that the increased temperature has triggered a transformation of the stacked triangles into clusters with a shape of a regular hexagon – the equilibrium shape which is expected from clusters stacked in the 2H sequence. Possibly, the formation of 2H-
MoS$_2$ is inhibited at the lower temperatures, resulting in the stacked triangles (Fig. 4.14). This may be a metastable situation caused by the smaller size of the clusters synthesized at these conditions. On the other hand, by raising the synthesis temperature, the cluster shape increases (area > 2000Å$^2$) and it appears that the stacked clusters are able to reach the thermodynamically stable stacking configuration and the predicted hexagonal shape. This is highly interesting in relation to the observation that stacked type II catalyst in general have a different reactivity than their single-layer type I counterparts [29,167]. The present results thus suggest that the stacked MoS$_2$ nanoclusters will have a size-dependent morphology, i.e. they behave quite differently from single-layer MoS$_2$ clusters which adopt only the triangular shape under sulfiding conditions.
Chapter 5

Chemistry of Single-layer MoS$_2$ Nanoclusters: Hydrogen

An understanding of how MoS$_2$ nanoclusters interact with reactants and intermediates is of vital importance in the attempt to unravel the nature of the active sites in HDS catalysis. As already discussed briefly in the introduction, only little direct knowledge is presently available on how S-containing molecules adsorb and react and the way in which hydrogen enters the catalytic reaction. The detailed description of the atomic edge structure of single-layer MoS$_2$ nanoclusters, opens up new possibilities for experiments in which the STM can be used to pinpoint active sites on the clusters and reveal signatures of reaction intermediates. In the next two chapters the interaction of hydrogen and thiophene (C$_4$H$_4$S) with MoS$_2$ will be investigated in order to identify possible active sites for adsorption and reaction on the triangular single-layer MoS$_2$ nanoclusters.

5.1 Interaction with hydrogen

Fully sulfided structures, like the triangular MoS$_2$ nanoclusters discussed in the previous section, are generally not believed to be the most active ones in HDS catalysis, since they appear to be sulfur-saturated and thus presumably incapable of strongly adsorbing sulfur bearing molecules to facilitate the catalytical exchange reaction with S. Before hydrodesulfurization can take place, the clusters need to be reduced with hydrogen and create sulfur vacancies, also termed coordinatively unsaturated sites (CUS), where Mo atoms have incomplete coordination to sulfur. In a simple description sulfur vacancies are in equilibrium with hydrogen and dihydrogensulfide gasses:

$$H_2(g) + S - \star \rightleftharpoons H_2S(g) + -\star,$$

where $-\star$ denotes a S vacancy. Evidently this reaction only describes part of the overall hydrodesulfurization scheme, but it is nevertheless regarded as one of the primary elementary and rate-limiting steps. In terms of a simple kinetic model, the equilibrium concentration of vacancies ($\theta_\star$) can be expressed as:
where $P$ denotes the partial pressure of hydrogen and dihydrogensulfide, respectively, and $\Delta E_S$ is the formation energy associated with the vacancy, which is negative if the vacancy formation is favorable. The equation merely states that a high ratio of $H_2$ to $H_2S$ combined with high temperatures favors the formation of vacancies, which will have a high concentration if the reaction is not too endothermic. While the external parameters are easily controlled, the $\Delta E_S$ is an inherent property of the catalytically active cluster and is consequently of considerable interest.

Both experimentally and theoretically it is found that S on the basal plane is bound very strongly ($\Delta E_S \approx 2.2$ eV) in accordance with the fact that the basal plane is highly inactive in HDS [67]. On the edges, sulfur atoms may be more or less tightly bound depending on the saturation under the actual conditions. A good catalysts is usually described by its ability to bind reactants or products with an intermediate strength (or else a high saturation will poison the active sites), but as will become clear shortly, it is not easy to determine exactly which kind of S coordination will lead to the most active sites. Sulfur vacancies, which are slightly unstable (around 0.5 eV) relative to the full coverage, seem to present such a scheme, but the nature of the vacancy is difficult to predict and observe since the S coverage on the edges depends on the exact experimental conditions. In the following, the model system consisting of gold-supported single-layer MoS$_2$ nanoclusters is exposed to hydrogen in order to investigate, in a controlled manner, the formation of S vacancies on the atomic scale.

5.2 Sulfur vacancies

When the fully sulfided triangular MoS$_2$ nanoclusters are exposed to hydrogen gas ($H_2$), STM images do not show any changes at the edges which can be related to vacancy formation. Even large exposures, up to 1100 L, in a background of $1.0 \times 10^{-6}$ mbar of $H_2$ with the sample kept at a temperature of 673 K do not facilitate the formation of vacancies on the triangular MoS$_2$ nanoclusters terminated by Mo edges with S dimers.

This apparent lack of reactivity of the fully sulfided clusters is most likely related to one or more rate-limiting steps in the detailed mechanism by which vacancies are formed. The reaction path leading to vacancy formation may be complex and involve dissociative adsorption of $H_2$, diffusion of $H$ species and formation and desorption of $H_2S$. Any of these steps can in principle inhibit the reaction, thus rendering the chance of capturing an event with the STM negligibly small. Specifically, the rather large dissociation energy of the $H_2$ molecule (4.52 eV) [168], may cause the reaction to be severely activated. The gap of at least thirteen orders of magnitude between real process pressures and the experimental conditions may then explain the apparent low possibility of reacting sufficiently activated hydrogen molecules with edge S atoms to form vacancies.

By reducing the MoS$_2$ clusters with highly active pre-dissociated hydrogen atoms (H), the reaction barrier associated with the formation of vacancies can be surmounted. This
so-called atomic hydrogen treatment is performed by placing the sample facing a glowing hot W filament and backfilling the chamber with gaseous hydrogen to a pressure of $1.0 \times 10^{-6}$ mbar in 5 minutes. In this way, small amounts of hydrogen molecules dissociate and find their way onto the sample [121, 169]. Prior to the dosage the sample is heated to 673 K and this temperature is maintained throughout the exposure by the close vicinity to the glowing T filament. After the exposure, the gas is pumped out of the chamber, the sample is cooled and finally transferred to the STM.

In terms of morphology of the MoS$_2$ nanocluster, STM images show that the highly reductive treatment changes only little. The clusters are still characterized as single-layer MoS$_2$ nanoclusters, with a predominant triangular shape, i.e. neither sintering or reshaping occurs by the treatment. However, from atom-resolved STM images, new features are observed at the edges which are associated with the formation of individual S vacancies. Typically one or two S atoms vacancies are created on the edges in each cluster. This is illustrated in Fig. 5.1 where the vacancies are imaged as regions on the edge with a depleted intensity. It is thus likely that the catalytically active sites in HDS are imaged for the first time on the atomic-scale.

It has been speculated that the vacancy formation can be assisted by distortions of the edge lattice and that rapid edge diffusion can lead to agglomeration of sulfur vacancies [29]. From a sterical point of view, such clustering of vacancies would be favorable for the adsorption of larger sulfur bearing molecules. Under the present conditions, the STM results show that (i) no severe distortions seem to be introduced in the vicinity of vacancies (ii) the vacancy diffusion is quenched at room temperature (iii) only isolated single vacancies are observed, i.e. no agglomeration occurs.

### 5.2.1 The nature of S vacancies

A straightforward geometrical interpretation of the vacancy depicted in Fig. 5.1 is a configuration in which a single S atom has been removed from a S dimer since the fully saturated Mo edge is the starting point (Fig. 5.2a,b). There are, however, circumstances which point in the direction that this intuitively simple picture does not hold and the edges are even more reduced.

First of all, the formation of single vacancies is seen to affect the atomic structure of the entire row of edge atoms in Fig. 5.1 (compare with the two other unreduced edges). This suggest either severe atomic relaxations or changes in the electronic structure associated with the one-dimensional edge states. If a grid is superimposed on the basal plane S atoms in Fig. 5.1, the positions of the vacancy holes on the edge correspond to positions which are shifted half a lattice constant, i.e. out of registry. Furthermore, line scans reveal that the average height of the outermost row of atoms on the reduced edges relative to the basal plane is shifted downwards by more than 0.5 Å, in contrast to the unreduced edges. Consequently, the corrugation along the remaining protrusions becomes almost extinct together with the characteristic double period of the S-dimer terminated Mo edges. With respect to the bright brim associated with an edge state, the general observation is that the brim near a vacancy is attenuated, although the brim near the vacancies in Fig. 5.1 seems to have disappeared almost entirely. This feature is, however, in the present case attributed to the close proximity of the two vacancies.
Figure 5.1: Atom-resolved STM image ($V_t = -8.5$ mV, $I_t = 1.12$ nA) of a triangular single-layer MoS$_2$ nanocluster after reduction with atomic hydrogen atoms at 673 K in 5 minutes. Image size is $46 \times 47$ Å$^2$. The location of two sulfur vacancies is illustrated with circles. The white dots show the registry of protrusions on the basal plane.
Figure 5.2: Vacancies on the Mo edge. **Left:** Ball models (side view) of the Mo edge illustrating different degrees of reduction. (a) Full coverage with S dimers terminating the edge (S dimer pairing is left out for clarity). From here the reduction can take two routes: (b) A single atom removed from a dimer to form a vacancy. (c) The S dimer is fully reduced to the Mo edge with monomers. (d) A vacancy is formed by removing a S monomer. **Right:** Energies associated with different degrees of sulfur coverage on the Mo edge of MoS$_2$. Compiled from 3 different theory sources [67,104,148,171]. All energies are defined from reaction 5.1 and are quoted with reference to the 100% coverage (S dimers), with negative values reflecting a more stable situation. The energies are calculated in a periodic supercell geometry and the values of the starred configurations represent only a singular vacancy in the limit where neighbor interactions or finite size effects can be neglected.

It will become evident in Chapter 7 that Mo edges covered with S monomers (Fig. 5.2c) are directly distinguishable in STM images from the fully saturated S-dimer terminated Mo edges. In particular it is shown both experimentally (Fig. 7.4) and theoretically in STM simulations (Fig. 7.6) that the monomer edge is imaged with a much lower intensity on the outermost protrusions, which consequently do not show any clear corrugation. Furthermore, the brim is weakened slightly. With this information in mind, it seems likely that the edges with vacancies (Fig. 5.1) reflect single S atom removed from a Mo edge which otherwise is terminated by S monomers. If the depleted regions on the edges in the STM images were reflecting vacancies created by removing a S atom on a dimer, it would be expected from symmetry that the defect should be formed on S dimer sites, i.e. on sites in registry with the S lattice, in contrast to the STM findings.

This is also the conclusion in a recent DFT study, where STM simulations of the Mo edge similar to Fig. 4.9 do not reproduce the features of the STM image if a vacancy is associated with one missing S of a dimer on the Mo edge [170]. Bearing this in mind, the vacancies imaged with STM are thus concluded to be single S atoms stripped from the Mo edge with monomers (Fig. 5.2d). Very recently, an STM simulation of an isolated edge vacancy on a triangular MoS$_2$ cluster terminated by the Mo edge with monomers was also reported by Schweiger et al., which is in qualitative accordance with Fig. 5.1.

What is, however, remarkable is the appearance of the two other edges in Fig. 5.1 which identifies with the Mo edge with S dimers, i.e. exhibiting edge protrusions out of registry, the bright brim and the double period. From a thermodynamical point of view it seems unlikely that some edges should be severely reduced by hydrogen to a coverage of less tan
50%, whereas others in the same cluster are left unreduced?

This was, however, the general observation in STM images and finds a possible explanation by a huge activation barrier associated with the disruption of the chain of S dimer pairs forming in the fully sulfur-saturated triangular clusters. In Section 4.7 it was demonstrated that the Mo edge with an even number of dimers always terminate the clusters (including Fig. 5.1). This extraordinary stability of a preferential number of S dimers, was speculated to be caused by a large energy gain ($\Delta E_{pair}$) associated with a lateral contraction of the S-dimers, thus forming S dimer pairs along the edge. The energy gain is a collective property of the entire row of S dimers, implying that the removal of one S atom from a dimer, which is required to make a vacancy, disrupts the entire chain of dimer pairs along the edge. It is likely that this step is associated with a high energetic barrier since the whole edge needs to reconstruct, and thus that the removal of the first S atom is strongly activated. No quantitative numbers are available at this point, but since the implications with respect to size and shape following the dimer pair formation are very pronounced in Section 4.7, it is speculated that the barrier is significant. A barrier exceeding $\sim 1.5$ eV implies that the first S atom is removed only on a few edges under the conditions of the experiment, in accordance with the STM findings 1. Once the barrier is surmounted and the first sulfur atom is removed by the atomic hydrogen, the chain of S dimer pairs is broken and each remaining S dimer on the edge can be reduced to monomers with a much lower activation energy.

It is stressed that the high activation energy is only associated with the removal of the first S atom on the entire row of sulfur dimers. Once the first S atom is removed from the chain of S dimers, a transition to a less coordinated edge (e.g. monomers) may thus proceed by the the reaction mechanism in 5.1 in which only the binding energy of each individual S atoms is considered. Several DFT studies [67,104,148,171], employing similar unit cells as the one illustrated in Fig. 4.8(a), have shown that the monomer configuration (Fig. 5.2c) is of equal stability to the dimer terminated edge, and thus the transition between the two should be easily realized by reduction in $H_2$. In fact, the energy diagram shows that the monomer is stable towards the dimer with $\sim -0.1$ eV. On the basis of the STM findings, it is concluded that this transition, although thermodynamically favored is highly activated due to the finite size effects, and can only be surmounted by dosing rather large amounts of pre-dissociated hydrogen.

Once the first S atom is removed from the chain of S dimers, it appears from the STM images that the reduction to S monomers proceeds without a significant barrier. A minimum value for the activation barrier of this further reduction of the edge from the fully sulfided to a 50% coverage can be estimated from the theoretical values of configurations (a) (b) and (c) in Fig. 5.2, where (b) is the activated state corresponding to a sulfur coverage between 50% and 100%. The relative energy of (b) compared to (a) is found to be on the order of 0.5 eV, i.e. the activated state can readily be surmounted to form the more stable S monomers under the conditions of the experiment, in accordance with the STM findings.

From the monomer configuration, S vacancies can then be created by further reduction, which is the situation imaged on one of the edges of the cluster in Fig. 5.1. The energy involved in creating a vacancy on the S monomer terminated Mo edge can be extracted from the graph in Fig. 5.2, and is found to be $\sim 0.6$ eV. Energetically, it is also seen from the graph that

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The rate (k) can be estimated by assuming typical Arrhenius behavior ($k = A \times \exp(-\Delta E_{pair}/kT)$ for the removal of the first S atom and a typical attempt frequency (A) of $1 \times 10^{13}$ s$^{-1}$.)
in Fig. 5.2 that the formation of many vacancies (approaching 0% coverage) is associated with a fairly high reaction energy, and this explains why only a few vacancies are seen and no agglomeration of vacancies occurs. Under ordinary HDS conditions the reaction energy is surmounted by the high pressures of H₂ and higher temperatures to ensure a reasonable population of the active sites. In conclusion, the active sites in the form of S vacancies on the edge of MoS₂ nanoclusters have been imaged for the first time directly on the atomic scale. It is, however, noted that it remains to be established whether the vacancies created on the Mo edges are the most active in HDS.

5.3 S-H groups

Another important aspect concerning the reactivity of the MoS₂ nanoclusters is the need for hydrogen to be dissociated prior to entering the catalytic hydrogenation of reacting molecules. The dissociation energy of the H₂ molecule is rather high (4.52 eV per molecule). However, in mechanistic studies of hydrogenation and hydrogenolysis of S-containing compounds, it is a common assumption that hydrogen has already dissociated somewhere on the catalyst surface, and that acidic S-H groups provide a source of reactive hydrogen atoms [29].

The actual state of hydrogen present on the MoS₂ catalyst particles is, however, controversial. This is related to the fact that the existence of S-H groups has been suggested only through indirect results from e.g. infra-red spectroscopy, raman spectroscopy or inelastic neutron scattering [29, 172, 173]. Again, the lack of direct structural information from such studies hampers a description of the nature and location of the S-H groups. The basal plane is observed to be inert with respect to hydrogen dissociation [67]. In infra-red spectroscopic investigations, Topsøe et al. found the formation of S-H groups to be associated with edge sites of single-layer MoS₂ nanoclusters. Although, vacancies are also formed here, this does not exclude that S-H groups coexist in the vicinity also. In fact, such a scheme may present a favorable situation from a chemical point of view, since adsorbed molecules may simultaneously interact with both vacancies and S-H groups.

The S-H groups can form through a simple equilibrium between gaseous hydrogen and edge S atoms:

\[
\frac{1}{2}H_2(g) + (S - \Box) \rightleftharpoons S - H_{ads}, \quad (5.3)
\]

where \( S - \Box \) denotes an empty adsorption site at the edges, and \((-H_{ads})\) the adsorbed H atoms. Associated with this reaction is the reaction energy \( \Delta E_H \), which is negative if H is bound to the cluster sites.

In the previous section focus was aimed at imaging the edge vacancies on the MoS₂ nanoclusters following exposure to highly reactive atomic hydrogen gas. However, in STM images the same experimental procedure is found also to facilitate the formation of S-H groups at the edges. Like the formation of vacancies, the reaction with molecular hydrogen gas (H₂) to form S-H groups is inhibited by the conditions of the experiment, and in STM images no change is observed, possibly due to the low chemical potential of H. So the formation of S-H groups does not seem to occur more readily than the creation of vacancies.
When the MoS$_2$ clusters are pre-exposed to atomic hydrogen, STM images, however, reveal new features at the edges which indicate S-H formation. Both reactions 5.1 and 5.3 consume hydrogen as a reactant, implying that these two are competing processes under reaction conditions. The selectivity of the catalyst determines the detailed branching of these reactions involving hydrogen, and Fig. 5.1 is a good example of a cluster exhibiting the result of both. Upon reduction with atomic hydrogen, the STM image of the cluster in Fig. 5.1 namely shows that one edge is reduced to the monomer edge and forms vacancies (Section 5.2) whereas the two other at first glance edges appear to retain the S dimer structure. It is, however, the observation from STM images that edges like these are found to adsorb hydrogen to form S-H groups.

Qualitatively, no structural change is seen on the two edges without vacancies in Fig. 5.1, i.e. protrusions are still out of registry and the brim associated with an edge state is retained. It is, however, the main observation from many atom-resolved STM images that the unreduced edges in clusters pre-exposed to atomic hydrogen have a small, but consistent intensity shift. By comparing the edges on the fully sulfided structures and an atomic hydrogen pretreated cluster, it is seen that the average height of the edge protrusions is shifted down relative to the basal plane by $\approx 0.2$ Å for the H treated cluster. This is illustrated in Fig. 5.3, where two representative STM line scans show the corrugation in a direction perpendicular to the edge. This downshift only occurs upon H-treatments, and it is therefore suggested that hydrogen adsorbs on the S dimers at the Mo edge of MoS$_2$ to form S-H groups. The resulting reduction in the intensity in STM images is attributed to a modification in the LDOS at the Fermi level in the interstitial regions between S dimers when H species saturate the edges.

Different configurations of S-H groups on the edges of MoS$_2$ have been extensively investigated in a recent theoretical study [104]. Of interest in the present context are the
5.3 S-H groups

Figure 5.4: S-H groups are formed on the edge, which is reflected in an intensity shift of the edge protrusion. (a) Top and side view of ball models showing the location of the H atoms on the S dimers of the Mo edge. Two H atoms (gray) adsorb on each dimer in a position slightly tilted perpendicular away from the edge and towards the basal plane. (b) A simulated STM image of the configuration in which S-H groups adsorb. Qualitatively, the STM image of this configuration changes little compared to the S-dimer saturated Mo edge (see Fig. 4.9), i.e. protrusions are out of registry and the bright brim retained. Quantitatively, the edge protrusions are shifted down by ~ 0.1 Å, in accordance with the STM observations. No substrate interactions with the Au(111) were included in the calculation.

configurations on the S dimer terminated Mo edge. Here, accordance with the STM results is found for a configuration in which H adsorbs on the S dimer in a position immediately adjacent to the bright brim, see Fig. 5.4(a). The figure also illustrates a simulated STM image generated using the Tersoff-Hamann theory on the basis of DFT calculations similar to those reported in Chapter 4. In agreement with the STM findings, the edges change little qualitatively, i.e. the high intensity of the brim is retained and edge protrusions reflect the interstitial space between S dimer with H adsorbed. Quantitatively, the simulated STM image also reproduces the downshift of the edge protrusions, although a slightly smaller value of ~ 0.1 Å is found. This difference may be attributed to substrate interactions which may influence the results. It is not expected that the deficiencies inherent to the Tersoff-Hamann approach are decisive here, since the two systems which are compared are geometrically very similar. Hence, it is concluded that the downshift observed with STM is due to H adsorbed on the S dimers.

In the adsorption configuration of H inferred from the STM images, the H atoms are, in fact, found to be marginally unstable relative to H₂ in the gas phase ($\Delta E_H = 0.03$ eV). In light of the almost athermic adsorption of H, it is tentatively suggested that an energy barrier prevents the adsorbed species from desorbing under the conditions of the experiment, and since this implies a similar barrier for dissociative adsorption of H₂, it also explains the need experimentally to pre-dissociate H₂. Additionally, the energies from the DFT are associated with some uncertainty, which could shift the sign of the adsorption energy.
Currently, calculations have also been initiated which will answer if the gold substrate has a significant impact on the binding of H to MoS\textsubscript{2} [170].

It is noted that no other adsorption configuration was found in the theoretical studies to be significantly more stable than the one found above, which is in accordance with other theoretical studies [174]. Furthermore, the alternative adsorption configurations of H in general induce geometrical or electronic changes which were not seen experimentally [170].

In conclusion, S-H groups are found to be present on the edges of the MoS\textsubscript{2} nanoclusters. Only by exposing the edges to atomic hydrogen, is it possible to absorb hydrogen in a metastable state on the edges. Consequently, the H atoms present on the edges are very reactive towards other adsorbed species, and thus provide a source of H. The next chapter will demonstrate how the S-H groups enter a hydrogenation reaction with thiophene (C\textsubscript{4}H\textsubscript{4}S) which leads to C-S bond cleavage – the first step of thiophene hydrodesulfurization. During industrial catalytic reaction conditions, the S-H groups are in equilibrium with gaseous hydrogen through reaction 5.3, and assuming a sufficiently high chemical potential of H, the edge will maintain a reasonable coverage of H. The use of atomic hydrogen in the present experiments can therefore be viewed as a simple way of providing hydrogen atoms at the high chemical potential found under industrial reaction conditions. In an experimentally controlled environment, the existence of S-H groups on the MoS\textsubscript{2} clusters could, in principle, be further studied by other surface science techniques employing vibrational spectroscopy, e.g. infra-red absorption spectroscopy (IRAS) or high resolution electron energy loss spectroscopy (HREELS) or maybe even sum-frequency generation (SFG) vibrational spectroscopy, which can be applied at high pressures. Such desirable studies, however, represent a big challenge due to the rather low number of adsorbed species and a presumably very low signal intensity – a fact which also explains why S-H species only have been observed indirectly in the real catalyst. The present results thus represent the first direct evidence of such species adsorbed on MoS\textsubscript{2} nanoclusters.
Chapter 6

Chemistry of Single-layer MoS$_2$ Nanoclusters: Thiophene

The molecular distribution found in petroleum fractions is very diverse with respect to size and structure, and the reactivity of the individual species in hydrotreating processes depends very much on such characteristics. To reach the required reduction in sulfur content of fossil fuels one has to react molecules with a lower and lower reactivity and it is therefore necessary to focus on the desulfurization of some of the most inert molecules [42,43,175].

In the present study thiophene (C$_4$H$_4$S) is investigated, with the aim of establishing fundamental insight into the interaction with the active MoS$_2$ particles. Thiophene is a simple and relatively inert S-containing molecule. A ball model of a thiophene molecule is depicted in Fig. 6.1. Thiophene is a five-membered aromatic compound with the S heteroatom embedded in a carbon chain containing two double bonds. Unlike open structures such as thiols (R-SH) or sulfides (R-S-R), the thiophene and especially substituted compounds derived from thiophene are very averse towards HDS, mainly due to additional stability of the S heteroatom in the aromatic structure, and exactly for that reason, thiophene is widely used to test the ability of a catalyst to remove S in the HDS process [29,176–178].

Despite intense efforts, the mechanisms and kinetics involved in thiophene hydrodesulfurization are still being debated extensively in the literature [29,39,179,180]. This is largely due to the uncertainties related to the nature of the active sites and the fact that reaction intermediates are very difficult to observe under reaction conditions due to hydrogenation and isomerization branching reactions [181]. Consequently, a large number of kinetic models have been proposed, the conclusions of which are often contradictory. Especially a clear identification of the rate limiting step(s) has not been established. As mentioned in the previous chapter, the creation of sulfur vacancies on the catalyst particles may be rate-limiting, but the rate associated with activation and subsequent bond scission of the C-S bonds in the molecule has equally well been argued to be important. On the microscopic level, the direct interaction of thiophene with the active clusters also remains controversial. Both electronic and sterical effects are important for adsorption of aromatic compounds like thiophene onto active sites. Using the nomenclature of organometallic chemistry, the
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![Figure 6.1: Ball model of the thiophene molecule (C$_4$H$_4$S, M = 84.1 amu) (S: yellow, C: black, H: gray). The molecular structure is also shown in a skeletal representation. The van der Waals size of the molecule is approximately 4x5 Å$^2$. In the pure form, thiophene is a clear, colorless liquid (mp = −38.2°C), with a very characteristic (foul) smell. The vapor pressure of thiophene is approximately 100 torr at room temperature, and the vapor can thus be admitted directly to the UHV.](image_url)

literature presents ample evidence for thiophene coordinated in modes involving $\eta^1$, $\eta^4$ or $\eta^5$ complexes and several more complicated ones [182–184], and a clear understanding of the controlling mechanisms is thus far from established. A more substantiated and direct investigation of the coordination of thiophene seems to be a prerequisite for a detailed elucidation of the controlling steps in HDS. In this section the scope is to investigate directly on the atomic-scale the interaction of thiophene molecules with single-layer MoS$_2$ nanoclusters.

### 6.1 Experimental details

The starting point is the well-characterized ensemble of MoS$_2$ nanoclusters synthesized by the standard preparation (Section 3.3). Experimentally, the dosing of thiophene is realized by a simple construction, in which gas phase thiophene is admitted through a doser to the UHV environment. Liquid thiophene (99% Aldrich) is contained in a glass tube at room temperature, and the thiophene vapor is admitted to the chamber by means of a leak valve. Furthermore, a stainless steel tube, which directs the flux of molecules directly onto the sample, is implemented in order to minimize contamination with thiophene in the UHV environment. This, however, limits the possibilities of achieving a calibration of the dosages applied, and no exact calibration of the doser was done. However, during thiophene dosage typical background pressures of $5 \times 10^{-8}$ mbar were used in a duration of 5 min, which is a large enough dosage to monitor a reaction. Prior to the experiments, the thiophene is further purified by freeze-pump-thaw cycles removing additional impurities like H$_2$O and dissolved gasses.

Experiments are conducted at sample temperatures in the range 180 K up to 500 K. Cooling was achieved by placing the sample in the STM, which allows the sample to reach temperatures below 140 K (see Section 2.2.1). However, line-of-sight between the thiophene doser and the sample placed in the compact STM is not possible, and during thiophene dosage the sample is picked up by a manipulator. This cannot be cooled, and, hence,
during dosage the sample temperature typically increases to 180 K before the dosage is complete and sample is repositioned in the cold STM. The temperatures quoted in this section thus refer to the maximum temperature achieved during low T operation. Similarly, during high temperature exposures, the sample is removed from the annealing heat source towards the thiophene doser. Consequently, the sample cools from the annealing set point, and for these experiments the lowest temperature is referred to as the experimental conditions.

To test the affinity of the Au(111) model substrate, thiophene was initially dosed onto the clean Au(111) surface at room temperature. No bonding at the terraces of the Au(111) was observed by the dosages applied in this study. This is in agreement with previous theoretical investigations [185] and a recent XPS study [186]. Additionally, this serves as a purity check of the thiophene vapor against contamination of e.g. thiols, which generally bind to the Au surface [187–189]. Only by exposing the surface to thiophene at sample temperatures below 180 K, did STM images reveal signatures of thiophene molecules adsorbed at the step edges of the Au(111) surface. However, even at these low temperatures thiophene molecules could not be observed on the terraces. This does however not exclude the possibility of rapidly diffusing molecules on the surface, which in general cannot be imaged with STM.

### 6.2 Thiophene adsorption on MoS$_2$ nanoclusters

Room temperature exposure of thiophene onto the freshly prepared single-layer triangular MoS$_2$ nanoclusters do not reveal any interaction. Indeed, the basal plane of MoS$_2$ [53] and the fully sulfided Mo edges appear to be inert with respect to thiophene. When lowering the temperature of the sample below 200 K, however, individual thiophene molecules situated near the edges of single-layer MoS$_2$ nanoclusters are observed in the STM images. As illustrated in the STM image in Fig. 6.2(a), thiophene molecules are imaged as large protrusions, the dimension of which ($\sim 4 \times 5 \text{Å}^2$) matches the expected van der Waals radius of thiophene. In fact, two different adsorption sites are inferred from the STM images: (i) on top of sites on the cluster in the vicinity of the edges (Fig. 6.2a), and (ii) thiophene is also found to decorate the cluster perimeter (Fig. 6.2a,b).

A rough estimate of adsorption strength of the two different adsorption modes of thiophene in Fig. 6.2(a) can be found in terms of their desorption temperature by heating the sample slightly in the manipulator and subsequent imaging of the sample in the cold STM. This is illustrated in the sequence of STM images Fig. 6.2(a)-(c) obtained of clusters at different substrate temperatures. The thiophene molecules decorating the perimeter (configuration (ii)) are seen to desorb at temperatures around 240 K ± 10 K indicating a relatively weak bonding concerned with this adsorption configuration. The slightly oval-shaped protrusions suggest that the molecules in both configurations are lined up along the symmetry axis of the molecule, i.e. with the sulfur of one molecule facing the end of the next. From the rather low corrugation of less than 0.4 Å above the Au(111), it appears that the thiophene is adsorbed in flat geometry on the Au(111) substrate. Possibly, this adsorption mode of thiophene is a result of dipole-dipole interactions with the cluster edge, combined with some sort of interaction between the $\pi$-system of thiophene and the Au substrate. Evidently, this binding of thiophene is of a non-covalent character and can be characterized as a physisorbed state of little relevance to the catalytic properties of the cluster. The weak bonding
is further underlined by a large distance to the outermost edge atoms of $\sim 4 \, \text{Å}$.

On the other hand, the thiophene species adsorbed on top of the basal plane (configuration (i)) can be attributed to a direct interaction between the thiophene and the cluster edges. Here, thiophene is even less tightly bound and is not imaged at temperatures exceeding $200 \, \text{K} \pm 10 \, \text{K}$. Interestingly, the sites where thiophene molecules adsorb seem to be associated with the bright brim, i.e. it appears to be a direct interaction with the metallic edge state of the Mo edge. In contrast to the common assumption that the fully saturated edges generally do not bind thiophene, the results clearly suggest that the special electronic environment present here facilitates the formation of stable chemical bonds. Again, a rather low corrugation and the position and dimension of the protrusions in Fig. 6.2 suggests that the nature of the bonding is associated with $\pi$-complexation at sites on top of the edge state. In the terminology of organometallic chemistry this corresponds to a flat $\eta^5$ adsorption geometry, which in this case not refers to coordination to a single metal atom but rather to a delocalized metallic edge state. Since heating the sample slightly above 200 K results in desorption of the molecules for the on-top site, it is concluded that this configuration is also a weakly physisorbed state and, hence, presumably of little direct catalytic relevance.

Thus, the fully sulfided MoS$_2$ nanoclusters terminated by Mo edges are found to only weakly adsorb thiophene from the gas phase. In the present context it should be noted, however, that the thiophene binds stronger to the metallic edge state than to the basal plane of the MoS$_2$ nanocluster. The low-temperature results thus provide information on a possible initial adsorption geometry of thiophene, which under the right conditions may lead to a HDS reaction.
6.3 Thiophene adsorption on H-activated MoS$_2$ nanoclusters

In the previous chapter it was shown by atom-resolved STM images that exposure to predissociated hydrogen atoms activates the single-layer MoS$_2$ nanoclusters: (i) by forming S vacancies on the Mo edges covered with monomers (Section 5.2) and (ii) by trapping H atoms on the edge to form S-H groups on the remaining S dimers (Section 5.3). The atomic hydrogen treatment is considered a simple way of providing hydrogen atoms at the high chemical potential found under industrial reaction conditions, and the STM findings may thus characterize the state of the catalytically active MoS$_2$ edges. It is therefore highly interesting to observe in the present study that only when the triangular MoS$_2$ clusters are pre-treated with atomic hydrogen a much stronger chemisorbed state of thiophene is observed in atom-resolved STM images, see Fig. 6.3, indicating a reaction of thiophene. In the following section, the reaction signatures observed in such STM images will be discussed and related to the vacancies and S-H groups as possible active sites for HDS.

Atomic H is produced by the same procedure as described in Section 5.1, and thiophene is dosed after the atomic H treatment while the sample is still hot. The exact temperature is found to be of little influence, and the adsorbed species were observed when thiophene was dosed at 350 K to 500 K. Subsequently, the sample was cooled to room temperature and transferred to the STM.

In Fig. 6.3 “bean-like” structures are observed in the row adjacent to the bright brim of the MoS$_2$ cluster. These can be associated with individual molecules bonded to the metallic edge state. From the line scans along the edge of the MoS$_2$ nanocluster in Fig. 6.4(a) and (b) it is furthermore concluded that the “bean-like” feature is always accompanied by a decrease in intensity (∼0.4 Å) at the edge protrusion located in front of the “bean-like” structure, and a slight increase (∼0.2 Å) of the two neighboring protrusions with respect to the Mo edge without the thiophene. Additionally, a closer inspection of the STM image (Fig. 6.4a) reveals that the “bean-like” feature is slightly asymmetric with respect to the corresponding edge depression.

As clearly demonstrated in the previous chapters of this thesis, STM images in general reflect a rather complicated convolution of electronic and geometric structure, and combined with the highly perturbed electronic structure at the edges of the triangular MoS$_2$ clusters, this makes it a difficult task to relate the observed structures in Fig. 6.4 to the molecular structure of reaction products or intermediates. It is, however, clear that the species in Fig. 6.3 do not reflect intact thiophene molecules coordinated to S vacancy sites, since the molecules are found to be very mobile, i.e. they can jump from one site to the next as imaged in consecutive STM images (see below). At no instance, vacancies were found to exhibit the same mobility at room temperature. Furthermore, the edges in Fig. 6.3 appear to be fully sulfided after the treatment, i.e. protrusions on the edge are out of registry and display the double period.

Thus, the direct end-on coordination of thiophene molecules to S vacancy sites cannot explain the STM findings. An alternative reaction scheme which involves the S-H groups can, however, account for the experimental observations. Evidently, the chemical properties

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1The dosing was done right after the H treatment to ensure a substantial amount of vacancies and S-H groups.
Figure 6.3: Atom-resolved STM image ($V_t = -331$ mV, $I_t = 0.50$ nA) of an atomic hydrogen pre-treated MoS$_2$ cluster subsequently exposed to thiophene. Image dimensions are $50 \times 54$ Å$^2$. The dashed circle indicates the features which are associated with individual molecules adsorbed at sites on the metallic edge state.
of the MoS$_2$ clusters change substantially upon exposure with atomic H, and it is proposed that the S-H groups play an essential role in a hydrogenation reaction of thiophene. From a chemical point of view, the highly reactive H atoms at the edges combined with adsorption sites of thiophene on the metallic brim (Fig. 6.3) presents a favorable situation for the hydrogenation of the double bonds and the resulting destabilization of the S heteroatom. In view of this, a compound in which either one or both the double bonds of thiophene have become hydrogenated seems to be the most likely candidate as the adsorbed species.

In order to rationalize this hypothesis and elucidate further the nature of the species observed in the STM experiments, extensive DFT calculations were recently performed by M. Nyberg at the Technical University of Denmark. In this study the Mo edge was again modelled by a single slab of MoS$_2$, and different molecules were adsorbed in a repeated geometry along the edges. In accordance with the low temperature STM experiments and earlier estimates of thiophene desorption temperatures on supported MoS$_2$ catalyst particles [183], it is found that pure thiophene indeed interacts very weakly with the fully sulfided edges of MoS$_2$. However, DFT calculations of several hydrogenated species derived from thiophene show that in particular a C$_4$H$_7$S\((cis\)-but-2-ene-thiolate) compound coordinated through the terminal sulfur atom to the edge S atoms near the brim is found to be very stable and shows a good accordance with the STM results. The adsorbed thiolates are illustrated in a simulated STM image Fig. 6.5(a) and the features associated with each molecule reproduce several of the most important features found in the STM image Fig. 6.5(b), including the shifted intensity of the three outermost protrusions near the molecular adsorption site. The
asymmetry of the “bean-like” structure behind the brim is also reproduced in the simulated STM images and is seen to be associated with the ring-opened carbon chain of the thiolate, the end-group of which is imaged with a higher intensity.

Figure 6.6 and 6.7 illustrates the proposed reaction pathway leading to the adsorbed $C_4H_7S$ state. Starting from the physisorbed thiophene (i) molecules ($E_{\text{ads}}$ less than 0.2 eV), one of the double bonds in thiophene is hydrogenated (HYD) causing the other double bond to move, i.e. 2,5-dihydrothiophene (ii) adsorbed to cluster edge is formed. In the next step, a calculation of the activation barrier is included in Fig. 6.7 for what is assumed to be the most difficult step in the reaction, the $C_\alpha-S$ bond cleavage. It is interesting to notice that the associated barrier is rather modest ($\sim 1$ eV). At the temperature (500 K) where thiophene is reacted, this means that equilibrium between $C_4H_7S$ and thiophene in the gasphase is easily achieved. The same is of course true at industrial hydrotreating condition. The barrier for the reverse reaction is, however, large enough for thiophene not to be desorbed during imaging at room temperature, in accordance with our experimental observation.

The final configuration (iii) associated with a ring-opened thiolate structure absorbed on the cluster edge is simply an ordinary thiol. After the $C_\alpha-S$ bond has been broken, the sulfur is much more reactive and the final extrusion may take place at another site on the cluster to complete the HDS process of thiophene.

Such sites are presumably sulfur vacancies located at the edges, as imaged on the Mo edge of the MoS$_2$ clusters in Section 5.2. It is likely that surface diffusion of the thiolates along the edge or through the gas phase to vacancies is needed for the final step in the overall reaction process. From the consecutive series of STM images illustrated in Fig. 6.8, mobility of the adsorbed thiolate species is indeed observed, supporting that the reactivity...
6.3 Thiophene adsorption on H-activated MoS$_2$ nanoclusters

Figure 6.6: The proposed reaction scheme of thiophene. All processes occur while the reactants are adsorbed on the fully sulfided edge of the MoS$_2$ nanoclusters. For clarity, only thiophene and H reactants are shown. The energies associated with the individual steps are shown below, extracted from a DFT calculation.

Figure 6.7: Energies associated with the reaction path (above) of thiophene species adsorbed on sites on the metallic edge state of MoS$_2$. The energies are in eV, and are calculated relative to gas phase thiophene and H adsorbed on the Mo edge ($\Delta E_{\text{fH}} \approx +0.03$ eV, see Section 5.3). The diagram displays the most relevant intermediate steps in the hydrogenation of thiophene and subsequent C$_\alpha$-S bond cleavage. Labels refer to the schematic representation above. The ball-and-stick models illustrate the geometric configurations associated with adsorbed species before, during and after C$_\alpha$-S bond cleavage (S: yellow, Mo: red, C: gray, H: white). The final configuration is C$_4$H$_7$S (cis-but-2-ene-thiolate). The position and geometry of the molecule adsorbed on the cluster is also illustrated in Fig. 6.5. Notice the modest activation barrier associated with the last step, (ii) to (iii), $E_a = 1.07$ eV.
Figure 6.8: (a) Sequence of STM images of the same MoS$_2$ triangle showing several adsorbed C$_4$H$_7$S species (each indicated with a black ellipse). The time lapse between images is on the order of one minute. In this time interval, individual species have moved to other sites on the cluster indicating one-dimensional mobility of the adsorbed species along the metal edge state.

can be explained by a two-step process. This mobility was also used to argue that the observed intermediates are do not reflect an interaction with vacancies which are immobile at room temperature. The final S extrusion is not observed directly in these dynamic STM movies, since the experiment, performed under UHV at room temperature, captures the model catalyst in a quenched situation, disabling the continued reaction of thiolates. Unlike during real HDS catalysis conditions, the number of available S vacancies is depleted once the atomic-hydrogen flux is terminated and thiophene is dosed due to the recombination of S from dosed molecules prior to imaging. However, by quickly cooling the sample in the STM to temperatures below 240 K after the thiophene flux was terminated, it was possible in a very few instances to capture species attached to the edge in a configuration that indicated a direct end-on bonding. This is illustrated in Fig. 6.9. Due to the low number of events and the inadequate quality of the images obtained of this, the identity of the adsorbed species has not yet been revealed.

To conclude, the STM results demonstrate the first direct atomic-scale information of thiophene HDS reactions on MoS$_2$ nanoclusters. A strong interaction is found to occur only when the clusters are pretreated with hydrogen, which suggest that acidic S-H groups change the reactivity of the clusters towards thiophene and leads to a hydrogenation reaction. The resulting species bonded to sites on the bright brim associated with a metallic edge state are identified as thiolates (C$_4$H$_7$S). Importantly, the formed thiols are much more reactive compared to thiophene and the full desulfurization may then occur on sulfur vacancies on the edges.

A new mechanism of the HDS reaction of thiophene on MoS$_2$ is proposed in which two significantly different sites are involved in first a hydrogenation (HYD) reaction and subsequent C$_\alpha$-S cleavage of one of the bonds in thiophene, possibly followed by S extrusion on a sulfur vacancy. In this way, an alternative two-step reaction path is offered by the clusters in contrast to the direct extrusion path of S in unhydrogenated thiophene on a S vacancy, which is the mechanism which receives the most substantial following on the literature. The hydrogenation sites are associated with one-dimensional metallic states at the edges of the fully saturated triangular MoS$_2$ nanoclusters, as observed in atom-resolved STM images. These brim sites are responsible for binding thiophene to the clusters and the hydrogenation reaction is driven by the nearby S-H groups which provide at source of highly reactive H
6.4 A new mechanism for HDS of thiophene on MoS$_2$

The STM observations have several important implications in terms of explaining the reactivity of MoS$_2$ nanoclusters. In particular, by identifying reaction intermediates a new route is identified for activating a relatively inert, sulfur containing molecule like thiophene. It takes place by hydrogenation (HYD) of the double bonds followed by a C$_\alpha$-S bond breaking. Remarkably, the completely sulfur-saturated Mo edge is able to not only hydrogenate the carbon double bonds in the presence of S-H groups but also to break the C$_\alpha$-S bond of the hydrogenated thiophene. All the processes take place on top of the sulfur atoms of the MoS$_2$ structure with no direct interaction with the Mo atoms. This interesting chemistry is associated with the metallic edge states of the MoS$_2$ nanocrystals, since no indication of chemical activity is found, experimentally or theoretically, at the S atoms on the basal plane of the MoS$_2$ structures. The metallic states associated with the edges, on the other hand, have the ability to donate and accept electrons and thus act as catalytic sites just like ordinary metal surfaces. While many catalytically active metal surfaces (Fe, Ni, Mo to mention a few [77, 190–193]) are poisoned by H$_2$S and strongly bonded sulfur residues, the metallic edge state of MoS$_2$ are clearly not. The metallic-like sites thus seem to offer a weaker albeit optimum bonding strength of sulfur in thiophene. This kind of interaction is a compromise having a cluster-adsorbate interaction of intermediate strength which characterizes a good catalyst [8, 69, 194, 195].

The picture that emerges of the reaction mechanism presented in this study thus suggests that prehydrogenation of thiophene adsorbed on the cluster is of crucial importance for the

![An STM image of an MoS$_2$ nanocluster first exposed to atomic hydrogen, then thiophene and imaged at 250 K. Possibly, the protrusion in the circle identifies with a thiophene or a hydrogenated derivative coordinated through the terminal S atom to a vacancy.](image)
catalytic processes occurring on MoS$_2$, since this destabilizes the S atom and facilitates the subsequent C$_\alpha$-S bond scission. In this context, it is worth pointing out that all of the previous considerations related to HYD or HDS of thiophene have been based on consideration of interactions with one or more under-coordinated Mo atoms. The present results mark a significantly different way of thinking of the reactivity related to the edges of MoS$_2$, since the HYD reaction may proceed at the unusual sites associated with the edge state on the fully sulfided edges.

One can estimate the rate of the reaction associated with the last step in Fig. 6.7 by assuming Arrhenius behavior. A barrier of $E_a = 1.07$ eV implies a turn-over-frequency of approximately $10^{13} \cdot \exp(-E_a/k_BT) \approx 10^5$ reactions per second at 673 K, i.e. the reaction into thiolates proceeds with a significant rate at typical catalytic operating conditions. The “traditional” way of thinking about the HDS reaction of thiophene is to contemplate direct coordination of the S to under-coordinated Mo atoms, i.e. on vacancies. The STM experiments do not exclude this possibility, and in fact the features observed at low temperature in Fig. 6.9 may equally well be a result of such end-on direct interaction of thiophene with a vacancy. It is therefore possible that both the direct extrusion of S in thiophene and the more elaborate mechanism suggested from the STM findings may prevail at operating conditions.

The co-existence of two active sites – one for hydrogenation (HYD) and another for the S extrusion (HDS) – inferred directly from the present atomic-scale studies explains the results of several other studies treating the kinetics and mechanisms of HDS catalysis [29]. Valuable information on the selectivity of the catalyst is obtained by selectively poisoning the active sites in the real catalyst with different molecules while simultaneously monitoring the reaction rates. In such inhibition studies, H$_2$S is in general found to severely inhibit the HDS reaction of thiophene, most likely due to vacancy recombination, whereas the HYD reaction of a long range of unsaturated organic compounds is found to be only slightly influenced. This simple observation can readily be explained by the new model of the reaction, since indeed H$_2$S is found not to adsorb directly on the sites associated with the edge state, i.e. it does not compete with the suggested active HYD sites$^2$.

On the other hand, the HYD activity of thiophene is observed to be severely inhibited during simultaneous reaction with more electronegative N-containing aromatic compounds like pyridine (C$_5$H$_5$N) or quinoline (C$_9$H$_7$N), implying that these molecules adsorb initially on similar sites as thiophene on the bright brim [29, 196]. Since the hydrogenation of such nitrogen-containing aromatics is also an integral part hydrotreating catalysis in the hydrogen-denitrogenation (HDN) process [29, 39, 197], it is therefore suggested that the chemical activity associated with sites on the metallic edge states of MoS$_2$ may be of general importance also for the wealth of other molecules present in crude oil. In future experiments it would be interesting to test this by exposing the clusters to other molecules and investigate the exact interaction of these.

Based on the present finding one can speculate whether the proposed two-step HDS reaction process of thiophene is also relevant for reactions of other and more complicated molecules present in the oil feed, and if so, whether it will be predominant. Whereas thiophene was chosen in this study since it represents a standard test-molecule, it does in fact not present the major obstacle in achieving deep HDS conditions. Substituted thiophenes

$^2$H$_2$S is abundant during synthesis and is not found to saturate sites on the bright brim. Likewise, in situ imaging of the triangular clusters in a H$_2$S atmosphere did not reveal H$_2$S adsorption.
6.4 A new mechanism for HDS of thiophene on MoS$_2$

(Fig. 6.10) like dibenzothiophene and especially the methyl substituted derivatives, e.g. 4,6-dimethyl-dibenzothiophene, present a much bigger problem due to sterical hindrance. For such molecules it is possible that the reaction path proceeding by prehydrogenation and bond cleavage is much more important than the direct extrusion, since the end-on coordination of S in the larger molecules is more sterically hindered than adsorption on the bright brim through a good overlap to the $\pi$-electron system. The suggested pre-hydrogenation route may lead to bond cleavage in the more complicated structures and thus lower the sterically hindered access to the S heteroatom. For even more complicated molecules all adsorption modes become sterically inhibited, and this explains the lack of reactivity in HDS for these. Herein lies the challenges for future improvements of HDS catalysts to accomplish deep HDS. To extend the present study, the adsorption of the more complicated S-containing molecules may reveal additional insight into the nature of the brim sites.

The present model also explains the suggestion of a previous study on structure-activity relationships. In the “rim-edge” model proposed by Daage and Chianelli [54], the catalytic clusters are described as stacked MoS$_2$ crystallites. Without discussing in detail the active sites responsible for HYD and HDS reactivity, they suggest that the top and bottom of the (unsupported) crystallites are associated with rim sites which are active in both the HYD and HDS reaction, whereas the edges in the intermediate layers are associated with HDS reactivity only. These results have a clear interpretation in terms of the new mechanisms presented above. Evidently, only the top layer of stacked MoS$_2$ clusters (see e.g. Fig. 4.14) will expose the metallic edge states, and hence will be active in HYD. Vacancies, on the other hand, will most likely be created both on the top but also on lower lying layers in such stacked structure, thus exposing sites which are primarily active in HDS.

In conclusion, a new model explaining the hydrotreating activity of MoS$_2$ is proposed, where two types of sites are involved and which is speculated to be applicable to HYD, HDS and HDN reactions of unsaturated molecules in general. Of special interest are the new active sites associated with one-dimensional edge states of MoS$_2$. These are quite unusual compared to the under-coordinated Mo atoms traditionally used to explain the reactivity of MoS$_2$ nanoclusters. The new insight is obtained by resolving both the electronic and atomic-scale geometric structure of nanosized MoS$_2$ clusters, the reactivity of which is probed by carefully monitoring the response to hydrogen and thiophene intermediates with STM. Like for the S-H groups in Section 5.3, it would be desirable to have the results verified by means of vibrational spectroscopy in a controlled experimental environment, e.g. by IRAS.
or HREELS, but again it is expected that the rather low number of adsorbed species results in low signal intensity and thus hampers a spectroscopy-based study.

The present study is another good example on how atomic-scale information can be achieved by investigating suitable catalysts model systems with the STM. The results demonstrate that one cannot neglect the cluster nature of the active materials in catalysts and model it from the usually well-known bulk properties. Atomic-scale insight is essential, and the experimental approach presented here should be applicable to inorganic clusters deposited on conducting substrates in general. Such detailed information may ensure a more rational way of developing e.g. new catalysts.
Chapter 7

Single-layer MoS$_2$ Nanoclusters in a Reducing Ambient

When establishing relations between catalyst structure and reactivity in idealized catalyst model studies, it is essential also to consider structural effects brought about by the operating conditions. Again, this is a matter which has been dealt with sparsely in HDS research, simply due to lack of suitable in situ characterization methods. A major factor influencing the cluster stoichiometry and structure is the gas composition used during the synthesis of the clusters. In fact, by setting up equations describing the thermodynamical equilibrium cluster shape from the Wulff construction (Fig. 4.3), the chemical potentials of sulfur and hydrogen enter through the partial pressures of $P_{H_2}$ and $P_{H_2S}$ into the edge free energies, and variations in the composition of the gasses may decisively influence the ultimate shape, sulfur coverage and adsorption of hydrogen species on the edges. Since the nature of the exposed active sites is intimately related to the morphology and edge structures, controlling the morphology means tailoring the reactivity of the clusters on the smallest scale. It is therefore of utmost importance to know the response of the active phase to the reactant gases.

With reference to the results obtained in previous chapters, it is possible with the STM to systematically vary the synthesis conditions and investigate effects on the morphology and edge structures of the single-layer MoS$_2$ nanoclusters. The triangular single-layer MoS$_2$ nanoclusters terminated by fully sulfur-covered Mo edges were synthesized under sulfidation conditions, i.e. in an atmosphere of only dihydrogensulfide. The aim in this chapter is to investigate the atomic-scale structure of the clusters, as more reducing conditions are approached during synthesis, since these are more reminiscent of typical HDS operating conditions where hydrogen gas is abundant. To rationalize the STM observations, the results are furthermore in an interplay with theory treated in an ab initio thermodynamic model, extending zero-temperature, zero-pressure DFT results to the finite pressures and temperatures of experiment and even to realistic HDS conditions.
Figure 7.1: A table illustrating the range in which the effect of gas composition is investigated. Conditions denoted with (*) are experimental with a total pressure of \(2 \times 10^{-6}\) mbar and a temperature of 723 K. The individual partial pressures of \(\text{H}_2\text{S}\) and \(\text{H}_2\) are ion gauge corrected values. For reference the typical HDS conditions at 650 K are also listed. To the right are values for the chemical potential of S and H adsorbed on the clusters quoted. The values a calculated relative to the chemical potential of elemental S and the energy of an isolated hydrogen molecule, respectively (see Section 7.4.1).

### 7.1 Experimental procedures

The effect of gas composition was systematically investigated by synthesizing the MoS\(_2\) clusters in several different gas mixtures, followed by detailed morphological and atomic-scale characterization of the surface structures with STM.

The main alteration compared to the standard preparation of the triangular MoS\(_2\) nanoclusters, is the shift from sulfiding the clusters in a pure \(\text{H}_2\text{S}\) gas to a synthesis which uses gas mixtures of \(\text{H}_2\) and \(\text{H}_2\text{S}\), i.e. with a reducing character. Hence, the main experimental tuning parameter during the synthesis of MoS\(_2\) is the ratio \(P_{\text{H}_2\text{S}}/P_{\text{H}_2}\). For reasons that will become clear below, the crystallization of MoS\(_2\) is furthermore performed at 723 K. Otherwise, the present study uses the parameters reported in Section 3.1 and follows the same steps as the standard preparation in Fig. 3.3.

Gases were dosed directly by backfilling the UHV chamber to the desired partial pressures of \(\text{H}_2\) and \(\text{H}_2\text{S}\). The \(\text{H}_2\text{S}\) gas doser implemented in the studies of the previous sections was abandoned in order to ensure an efficient mixing of the two different gasses near the sample and to have an exact measure of the gas composition at the sample. The flexibility range of experimental gas compositions in terms of the ratio is limited by constraints imposed by equipment and conditions of the experiment, since (i) a minimum \(\text{H}_2\text{S}\) partial pressure is required to fully sulfide the MoS\(_2\) structures, and (ii) the integrity of the UHV system limits the maximum achievable total pressure. Additionally, \(\text{H}_2\text{S}\) dosed from a lecture bottle has a nominal purity 99.8% with hydrogen being the major impurity. Hence, the effect of gas composition is investigated with the fraction \(P_{\text{H}_2\text{S}}/P_{\text{H}_2}\) in an interval (see figure 7.1) from approximately 500 to 0.06 with a total pressure of \(1 \times 10^{-6}\) mbar (ion gauge corrected values are used). This was, however, sufficient to observe a clear effect in STM images of the clusters. It is implicit from the conditions listed in the table that the partial pressure of \(\text{H}_2\text{S}\) varies in the experiments, but the large dosages used were in all cases observed to result in fully sulfided MoS\(_2\) clusters.

For reference, typical HDS operating conditions are also listed in the table in Fig. 7.1. Operating HDS conditions are usually more reducing than what is investigated in this study,
combined with, of course, pressures many orders of magnitude higher. Nevertheless, the present results demonstrate certain trends, which may be useful in a characterization of the working HDS catalyst.

Surface structures crystallized in a fully sulfiding atmosphere at 723 K are chosen as a reference for the results reported here (compared to 673 K of the standard preparation), since the effect of gas composition at this temperature is most clearly illustrated from surface morphology in this case. As discussed in Section 4.9, the Au substrate temperature during crystallization is also a major issue, which, due to agglomeration, affects the morphology under the conditions of the experiments. The reason why a slightly higher postanneling temperature reveals the trends more clearly is explained by the larger size of clusters synthesized in this way (~650 Å²) and the fact that finite size effects tend to have a smaller impact on these. This will be discussed in detail in Section 7.5. When crystallizing the MoS₂ at 723 K the majority of the clusters are, however, still predominantly triangular under sulfiding conditions (see e.g. Fig. 4.12), and as will be evident in the next section, the ensemble still represents a good reference benchmark in the present experiments when synthesizing in a reducing ambient.

### 7.2 Hexagon-shaped MoS₂ nanoclusters synthesized in a reducing ambient

This section reports on three experiments investigating the response of the morphology and edge-structures of single-layer MoS₂ nanoclusters to gas atmospheres denoted as sulfiding, intermediate and reducing as listed in Fig. 7.1. By increasing the fraction of hydrogen (H₂) during the synthesis of MoS₂ nanoclusters on Au(111), STM images of the cluster morphology reveal a gradual transition of the cluster shapes. Unlike at pure sulfiding conditions, triangular shapes cease to dominate and eventually disappear totally when the ambient becomes reductive. This is combined with the emergence of what appears to be a new preferential shape, i.e. hexagon-shaped MoS₂ nanoclusters (Fig. 7.2). The height of the predominant structures still corresponds to single-layer MoS₂ structures (e.g. ~2.1 Å at V_t = -1250 mV). Hence, it is concluded that the shape of the single-layer MoS₂ nanoclusters is dependent on the P_H₂S/P_H₂ ratio.

The measured distribution of shapes for the three preparations is illustrated in Fig. 7.3 and the diagrams reveal the details of the structural transition as the hydrogen fraction is increased. For all three experiments the average cluster size is constant around 650 Å², which excludes that shape changes occur due to enhanced gas-assisted agglomeration. Under sulfiding conditions (99.8% H₂S), the preferential shape is seen to be the triangle. More than 55% are characterized as equilateral triangles with the rest being metastable structures. At the intermediate conditions (25% H₂S), the morphology is observed to be rather inhomogeneous, with no prevailing unique shapes. The morphological transition is, however, clear when moving towards even more reducing conditions (7% H₂S) where the majority (> 55%) of structures are characterized as hexagon-shaped MoS₂ clusters suggesting that this is now the equilibrium form of single-layer MoS₂.

For an ensemble of clusters to be considered as equilibrium structures they must all, in principle, have a unique shape according to the Wulff construction (Fig. 4.3), i.e. a constant
ratio of edge free energies. The situation is, as Fig. 7.2 suggests, not as clear-cut, and no unique value of $\gamma_S/\gamma_{Mo}$ seems to characterize the clusters. The occurrence of such clusters does, however, not necessarily mean that the clusters are metastable structures resulting from kinetic limitations during growth. Indeed, the predominant clusters can in this analysis be categorized as shapes which appear with the symmetry predicted from the Wulff construction of MoS$_2$, but not necessarily with a unique edge free energy-ratio. On this basis, it is therefore concluded that a hexagonal form appears to be the equilibrium shape of MoS$_2$ nanoclusters under the reducing conditions of the experiment.

The co-existence of two types of edge terminations, i.e. the (1010) Mo edge and the (T010) S edge, is an immediate consequence of the predominant hexagonally truncated shape of the single-layer MoS$_2$ islands (Fig. 1.6). In the present context, the synthesized ensemble of hexagon-shaped MoS$_2$ nanoclusters thus enables a direct investigation of the S edge also. Metastable MoS$_2$ structures like the trapezoids or pentagons also exhibit the S edge, but the approach presented above demonstrates a fully reproducible way of synthesizing equilibrium structures, which may be relevant at HDS conditions.
Figure 7.3: The shape distribution of single-layer MoS$_2$ nanoclusters, synthesized at 723 K using three different gas compositions, going from predominantly sulfiding (left) to reducing conditions (right). The shapes are organized in three categories: triangles (black), metastable structures such as e.g. trapezoid or pentagons (gray) and hexagonal structures (light gray).

7.3 Edge structures of hexagonal MoS$_2$ nanoclusters

An atom-resolved STM image of a hexagon-shaped single-layer MoS$_2$ nanocluster synthesized under reducing conditions is displayed in Fig. 7.4. On the basal plane of the cluster, protrusions are still imaged with a hexagonal symmetry and an interatomic distance of $\sim 3.15$ Å representative of the topmost S layer of MoS$_2$. The cluster is imaged with two considerably different types of edges, each associated with either the Mo edge or the S edge. Interestingly, neither of these have the characteristics of the Mo edge with S dimers, which was found in the triangular MoS$_2$ nanoclusters under sulfiding conditions, i.e. new edge structures seem to be favored.

7.3.1 The Mo edge with S monomers

In the hexagonal MoS$_2$ cluster illustrated in Fig. 7.4 one of the two edge types is associated with a very low intensity at the outermost row. The edge is also characterized by a similar striking brim as previously shown to be associated with one-dimensional metallic electron-states at the Mo edge. The height of the brim above the basal plane is measured to be $0.25 \pm 0.10$ Å, i.e. a little smaller than for the Mo edge with dimers. For comparison, the graph in Fig. 7.5 shows an STM line scan perpendicular to this type of edge in the hexagon-shaped cluster and the equivalent scans for a cluster terminated with S dimers on the Mo edge. The line scan for the former shows that the height of the edge falls off rapidly as the brim is crossed. The lack of corrugation in the STM images, implies that the LDOS at the Fermi level at this edge is vanishingly small.

Concerning the identity of the edges of the hexagon-shaped clusters synthesized under reducing conditions, edges with a lower coverage of sulfur than the fully saturated dimer-covered edges should be considered. Especially, the Mo edge with monomers (Fig. 7.6a) is a candidate, since it is of equal stability to the fully covered edges (Fig. 5.2), and in the absence of a high chemical potential of sulfur during synthesis, edges with this lower (50%) S coverage may be favored.
Figure 7.4: (a) Atom-resolved STM image ($V_t = 39.1$ mV, $I_t = 0.31$ nA) showing a typical hexagon-shaped single-layer MoS$_2$ nanocluster synthesized under reducing conditions (7% H$_2$S). Image dimensions are $27 \times 28$ Å$^2$. The position of the protrusions on the basal plane and S edge are marked with white dots.

To rationalize the experimental observations, the characteristics of the edges from the STM image are compared with a simulated STM image of the Mo edge with S monomers in Fig. 7.6(c). The simulated STM image was generated using the Tersoff-Hamann theory in a similar fashion as in Section 4.5 and based on the electronic structure output from elaborate DFT calculations employing a slab-geometry of MoS$_2$ which exposes both the Mo edge with monomers at one end and the S edge at the other end (Fig. 4.8). Furthermore, the effect of the Au(111) substrate is included.

The simulated image of the Mo edge terminated with S monomers is seen to reproduce the details in the STM image. Especially, it is noticed that the outermost S atoms are not imaged at all, i.e. the LDOS at the Fermi level is zero here. The reason is that the Fermi level in this case is not crossed by any electronic states pertaining to the Mo edge, i.e. the monomers on the Mo edge are locally semiconducting. The fact that the edge is not metallic does not exclude the existence of edge states on the Mo edge, and the bandgap near the edge is in fact found in calculations to be considerably reduced compared to the bulk, implying
7.3 Edge structures of hexagonal MoS$_2$ nanoclusters

7.3.1 The Mo edge

The existence of such. The simulated STM image also reproduces the bright brim extending along the row behind the S monomers, and it is therefore concluded that the Mo edge of the MoS$_2$ hexagons synthesized under reducing conditions are terminated by S monomers. Apparently, the stability between the monomer and dimer coverage has shifted in favor of the monomers by introducing the reducing conditions of this experiment.

7.3.2 The S edge

The other, more intense edges of the hexagon-shaped MoS$_2$ nanocluster in Fig. 7.4 are from the symmetry of MoS$_2$ associated with the S edges. Here, protrusions on the edges are clearly imaged, and by superimposing a grid on the basal plane S atoms, they are observed to be in registy. Associated with the S edges, is also a rather intense bright brim adjacent to the outermost row of protrusions. The corrugation of the brim above the basal plane is found to be 0.5 Å ± 0.1 Å. Unlike the brim on the Mo edge, which seems to be smeared out along its direction, the corrugation along the S edge brim is rather pronounced with protrusions imaged with the characteristic 3.15 Å periodicity of MoS$_2$.

If it is tentatively assumed that the brim and edge protrusions reflect the position of S atoms on the S edge, judging from their position it then appears that the S edge in the clusters is the result of a simple continuation of the bulk MoS$_2$ lattice (see Fig. 1.6). This straightforward interpretation is, however, not corroborated in simulated STM images. Like
the fully covered Mo edge, the S atoms on the S edge are found to dimerize along a direction perpendicular to the cluster plane [67, 104, 148], and for this configuration, the brim is found in simulated images to extend all the way to the outermost protrusion in clear contrast to the STM findings [105, 170]. Also S edges with a reduced coverage (75%, 50% sulfur) do not account for the STM findings since both of these configurations exhibit a very clear double period superstructure along the edges and are additionally found to be energetically unstable in DFT studies. An example of a simulated STM image of the latter half-saturated S edge is given in Ref. [105].

A fully covered S edge with hydrogen atoms adsorbed on the S dimers is, however, found to match the STM images and is furthermore found to be energetically very stable. A large number of possible adsorption sites for H on the S edge have been investigated [104, 174], and in contrast to the Mo edge (Section 5.3), H is found to bind strongly to the S edges. A ball model of the most favorable adsorption configuration is illustrated in Fig. 7.7(a). Hydrogen atoms are found to adsorb preferably on the edge S atoms only on one side of the cluster in a position slightly behind the outermost row towards the basal plane. The adsorption energy is rather large, $\Delta E_{HH} = -1.26eV$ for each hydrogen$^1$. The strong adsorption of hydrogen is seen to split the S dimers apart which is shown in the ball

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$^1$The energy of adsorption is defined from reaction 5.3 in Section 5.3.
7.3 Edge structures of hexagonal MoS$_2$ nanoclusters

Figure 7.7: (a) Ball models of the fully sulfided S edge, shown in side (left) and top view (right). By adsorbing H (gray) ($\Delta E_H = -1.26$ eV) the S dimers are broken and S-H groups are formed on top of the cluster edge. (b) Electronic structure illustrating the metallic edge state of the S edge with hydrogen adsorbed ($\text{III}_H$, red lines) crossing the Fermi level at $k_F \approx 0.15$ Å$^{-1}$. States I and II belong to the Mo edge with dimers which in this particular calculation terminates the other end of the supercell. For consistency, the S edges with dimers without H adsorbed were also investigated (green, dashed lines). The electronic state III pertains to this edge S edge, which, however, is not observed in the experiment. (c) A simulated STM image showing the S edge terminated in the way illustrated in (a). The calculations were done for an MoS$_2$ slab on Au(111), and Mo and S atoms are represented in the background as large and small balls, respectively.

Indeed, all the experimentally observed features are reproduced in the simulated STM image in Fig. 7.7(c) of this configuration. Here, the outermost protrusions are associated with the S-H groups forming on the upper row of S atoms. In the row behind, a pronounced bright brim is also seen, which is associated with a metallic edge state of MoS$_2$, now pertaining to the S edge. The edge state can be observed in Fig. 7.7(b), where the band structure of the S edge with hydrogen adsorbed is shown. Compared to the bands associated with states at the S edge with no hydrogen adsorbed (III), the band associated with the present structure ($\text{III}_H$) changes by the splitting of the dimerized S atoms, and is seen to become truly metallic, crossing the Fermi level at $k_F \approx 0.15$ Å$^{-1}$. The wave functions corresponding to the one-dimensional metallic edge state is found to be characterized primarily by the bond between the $p$ orbital on the lower S atom in the dimer, and the Mo $d$ orbital in the adjacent row.
Hence, it is found that the S edges, terminating the hexagonal MoS$_2$ nanoclusters synthesized in a reducing ambient, are terminated with S dimers covered with hydrogen. In an interplay with DFT, the most stable adsorption site of H is revealed, and the results thus represent direct evidence of such species strongly adsorbed on the catalyst. This is important since H species are expected to enter the catalytic reaction, e.g. in a hydrogenation reaction. To conclude, it is found on the basis of the STM images that single-layer MoS$_2$ clusters synthesized in a reducing atmosphere adopt a hexagonally truncated shape and are terminated by the Mo edges with monomers and hydrogen-covered, fully sulfur-saturated S edges.

7.4 Approaching HDS conditions: *ab initio* thermodynamics

Having established the morphology and edge stoichiometry under the reducing conditions of the experiment, the conclusions can be taken one step further and are in the following discussed in terms of a thermodynamic model, where the zero-temperature, zero-pressure DFT results are extended to the finite pressures and temperatures of this experiment. This serves to investigate in further detail the nature of the edges and allows for the results to be extended to realistic HDS conditions.

The general methodology used in the following analysis has previously been applied to catalytically relevant systems like the Al$_2$O$_3$ [199], Fe$_2$O$_3$ [200] and RuO$_2$(110) surfaces [201] as well as MoS$_2$ edges [105, 148, 171, 174]. The approach relies on expressing the edge-, or surface free energies in terms of their DFT energies and the chemical potential of the involved species. By careful consideration of the gas-surface equilibrium, the resulting *ab initio* thermodynamics can thus be used to address surface composition in different scenarios with varying chemical potentials of reactants and products. In the phase-space of possible MoS$_2$ edge stoichiometries, the experimentally observed structures of this study serve as fix-points for a validation of the model. Extrapolated to the technologically relevant conditions of high temperature and pressure, the model may thus also reveal if the experimental situation describes in sufficient detail the state of the catalyst, i.e. bridges the pressure gap in catalysis.

7.4.1 Thermodynamic model

In the following, the thermodynamic model used to investigate the nature of the MoS$_2$ edges at different ambient conditions is briefly outlined. All DFT calculations are performed for MoS$_2$ on Au(111). The full details of a similar thermodynamic treatment on an unsupported MoS$_2$ slab are given in Ref. [104].

The basis of the model relies on an expression of the edge free energies associated with single-layer MoS$_2$. Since the DFT energies are derived from slab calculations where the unit cell exposes both edges (see Fig. 4.8), the individual edge free energies of the Mo edge and S edge cannot be extracted directly from this analysis and an average value must be used. For an MoS$_2$ slab exposing the S edge and Mo edge, the average edge free energy ($\gamma$)
can be approximated as:

\[
\gamma = \frac{1}{2L} \left[ E_{\text{DFT}}(\text{MoS}_2 + N_H H) - N_{\text{Mo}} E_{\text{bulk MoS}_2} + (2N_{\text{Mo}} - N_S) \mu_S - N_H \mu_H \right] \tag{7.1}
\]

where \( E_{\text{DFT}} \) denotes the \textit{ab initio} DFT energies of the calculational unit cell with composition \((\text{MoS}_2 + N_H H)\), \( E_{\text{bulk MoS}_2} \) is the energy of bulk MoS\(_2\), and \( N_i \) is the number of atoms within the computational unit cell. \( L \) is the length of the edge. The factor of two in equation 7.1 indicates that \( \gamma \) represents the average value of both edge free energies. A trick is implemented in order to extract variations in the edge free energies as the stoichiometry of either one of the edges changes; by fixing one of the edge terminations in a given stoichiometry, the changes in the energetics of the other can be investigated by systematically varying its composition with respect to S and H coverage.

The Mo and S edges will maintain a coverage of S and H atoms which depends on the exact conditions. The effect of the gaseous ambient enters the equation of the edge free energy by the chemical potentials of S on the surface (\( \mu_S \)) and adsorbed H species (\( \mu_H \)) through the reactions:

\[
H_2(g) + S - \ast \rightleftharpoons H_2S(g) + -\ast, \tag{7.2}
\]

and

\[
\frac{1}{2} H_2(g) + (S - \Box) \rightleftharpoons S - H, \tag{7.3}
\]

where \( \ast \) and \( \Box \) denotes adsorption sites for S and H respectively. The values of the respective chemical potentials can be evaluated by consideration of the reactions above and from general thermodynamic properties of the gasses.

\[
\mu_S = \mu_{H_2S} - \mu_{H_2} \quad \text{and} \quad \mu_H = \frac{1}{2} \mu_{H_2}. \tag{7.4}
\]

Assuming that the gasses are ideal, the chemical potential of S (\( \mu_S \)) depends on the conditions through the temperature (T) and the individual partial pressure of \( H_2S \) and \( H_2 \) by their ratio and is as such independent of the total pressure:

\[
\mu_S(T, P) = \mu_{H_2S}(T, P^0) - \mu_{H_2}(T, P^0) + k_B T \ln \left( \frac{P_{H_2S}}{P_{H_2}} \right), \tag{7.5}
\]

where \( P^0 \) is a reference value of the pressure. The second chemical potential of adsorbed hydrogen (\( \mu_H \)) is furthermore seen to depend on the total pressure \( P_{H_2} \) by:

\[
\mu_H(T, P) = \frac{1}{2} \left[ \mu_{H_2}(T, P^0) + k_B T \ln \left( \frac{P_{H_2}}{P^0} \right) \right], \tag{7.6}
\]

By assuming thermodynamic equilibrium, and by choosing the reference value \( P^0 = 1 \) bar, the chemical potentials of the gasses can be found in standard thermodynamical tables and \( \mu_S \) and \( \mu_H \) may be estimated for any given set of conditions. However, the quantities cannot be evaluated without bounds. The chemical potential \( \mu_S \) is restricted to a limited range, in which MoS\(_2\) in one extreme is reduced to metallic Mo and another where elemental sulfur (\( S_{\alpha} \)) is formed on the surface. The chemical potential is thus calculated with reference to
the chemical potential of elemental sulfur. Similar boundaries can be defined for \( \mu_H \) which is calculated relative to the energy of an isolated \( H_2 \) molecule.

Returning to equation 7.1, the stable edge structures of MoS\(_2\) for a given set of chemical potentials \( (\mu_S, \mu_H) \) will be the one that minimizes the edge free energy \( (\gamma) \). A phase diagram can then be constructed as a function of \( \mu_S \) and \( \mu_H \) by mapping out the most stable configurations with S and H adsorbed on the MoS\(_2\) edges. The result is shown in Fig. 7.8, where the stability regions of the MoS\(_2\) edge stoichiometries (indicated with legends) are separated with boundaries. A phase diagram is shown for both the Mo edges and S edges, separately.

To manoeuvre around in the phase diagram one needs to know all the parameters entering equation 7.5 and 7.6, i.e. the temperature (T) and the partial pressures \( (P_{H_2S} \) and \( P_{H_2} \)) and it is consequently not possible to substitute the chemical potentials on the axes by simple experimental parameters such as e.g. only the partial pressures. To get a feeling of the response by changing the parameters, one can, however, state certain trends. Noticeably, the effect of changing the partial pressures of \( H_2S \) and \( H_2 \) at constant temperature is indicated by arrows in the phase diagram since these are the main tuning parameters in the STM experiments, but it is emphasized that temperature and total pressure also play a role.

In table 7.1 the chemical potentials \( (\mu_S, \mu_H) \) are calculated corresponding to the STM experiments performed at the two extreme situations, viz. sulfiding and reducing conditions at 723 K, respectively. These experimental points are also plotted in the phase diagram as dots. Their positions in relation to the STM observations will be the subject of the next sections. A complicating factors is, however, the “quench-and-look” nature of the STM experiments since the synthesis and subsequent imaging occur at different conditions. It is therefore not a priori clear to which extent the edge stoichiometry is changed as the conditions are gradually shifted from synthesis to imaging conditions (UHV, room temperature), and it is necessary to consider a range of parameters concerned with each of the two experiments. Hence, for the two experimental conditions (synthesis in sulfiding or reducing atmospheres) two extreme points are indicated each representing the chemical potentials during synthesis (Red(1) and Sulf(1)) and the conditions during subsequent STM imaging (Red(2) and Sulf(2)). The chemical potentials at imaging conditions were estimated at 300 K and with (low) partial pressures of \( H_2S \) and \( H_2 \) registered from the background composition after the synthesis\(^2\). The points corresponding to sulfiding conditions are not plotted in the phase diagram of the S edge since under these conditions the triangular MoS\(_2\) nanoclusters were found to expose Mo edges exclusively.

If a phase transition is predicted to occur when imaging conditions are approached after the synthesis, two things can happen: Either the degrees of freedom are frozen out and the clusters are imaged as synthesized, or the kinetics associated with the phase transitions are favorable, and in this case the edge structure is changed. This could, for example, happen through adsorption/desorption processes as the sample cools and UHV is achieved. The phase diagrams in Fig. 7.8 will be related to the STM observation in the next sections. First the Mo edge is treated.

\(^2\)Generally more hydrogen was present after synthesizing in a reducing ambient explaining why the two points Red(2) and Sulf(2) do not coincide.
7.4 Approaching HDS conditions: *ab initio* thermodynamics

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**Figure 7.8:** (a) The phase space of stable edge stoichiometries of the Mo edge (upper) and S edge (lower). The axes represent the chemical potential of sulfur and hydrogen calculated from equations 7.5 and 7.6. The points Sulf(1) and Red(1) refer to the experimental sulfiding and reducing conditions, respectively, and the points Sulf(2) and Red(2) refer to the STM imaging conditions under UHV and room temperature. The arrows indicate the influence of partial pressures of H$_2$S and H$_2$ for constant temperature. The phase diagram is calculated for an MoS$_2$ slab supported on Au.
7.4.2 Thermodynamic stability of the Mo edge

Under sulfiding conditions, the triangular MoS$_2$ nanoclusters terminated by Mo edges were found in atom-resolved STM images to be saturated with sulfur, i.e. sulfur dimers (Chapter 4). In accordance, the S dimers are found to be favored at the Mo edge under a high chemical potential of S and low chemical potential of H, corresponding to the sulfiding conditions used in the standard preparation shown in the phase diagram for the Mo edge. The dimers are observed to be stable in the phase diagram irrespective of whether the conditions are synthesis parameters Sulf(1) or during STM imaging Sulf(2).

When synthesizing the MoS$_2$ nanoclusters under reducing conditions, atom-resolved STM images of the hexagonal MoS$_2$ nanoclusters show that the Mo edges are covered with S monomers (50% S coverage). The point Red(1) in the phase diagram corresponds to these conditions. When the partial pressure of H$_2$ during synthesis is high, the chemical potential $\mu_S$ is low, and the point representing these synthesis conditions is seen to be situated well inside the region where the monomers are stable, in accordance with the STM findings.

At imaging conditions Red(2), the point in the phase diagram lies close to the transition line between the phase regions characterized by dimers (100%) and monomers (50%), i.e. it is in principle a possibility that the dimers have become thermodynamically stable again. As Fig. 7.4 suggests, this was not the general observation. This may be related to a significant kinetic barrier associated with the transition from monomers to dimers. Evidence of such an apparent barrier associated with the edge restructuring is provided by further STM experiments, where the hexagon-shaped MoS$_2$ clusters are re-sulfided with H$_2$S. Simply exposing the clusters to gaseous H$_2$S corresponding to a background pressure of $1 \times 10^{-6}$ mbar did not result in the formation of dimers, despite the large chemical potential of S and the fact that dimers are favored at sulfiding conditions. Only by activating the process by heating to 573 K could the S dimers be formed on the Mo edges of the hexagonal MoS$_2$ clusters, indicating that a substantial energy barrier is associated with the structural transition from monomers to dimers. An example of a re-sulfided hexagon-shaped cluster is depicted in Fig. 7.9(a), where the signatures of the Mo edge with dimers are clear on the longer edges, i.e. edge protrusions imaged out of registry.

The observation that the monomer-to-dimer transition is activated is in accordance with the discussion related to the formation of S vacancies on the Mo edge (Section 5.2) where the reverse transition from dimers to monomers (and thus vacancies) was suggested to be energetically highly activated as well. This may be related to the fact that the S monomers on the Mo edge are reconstructed (out of registry) relative to the dimers (Fig. 4.5) implying that a transition between them requires a long-range rearrangement of the S adsorbates probably involving several intermediate steps. If the transition is thus hindered by kinetic effects, the Mo edge structures observed with STM will be determined by the conditions during synthesis rather than during imaging, in accordance with the STM findings.

Interestingly, both monomer- and dimer-terminated Mo edges are in some clusters found to co-exist when they are synthesized at the intermediate conditions (25% H$_2$S). The corresponding point in the phase diagram (Int(1)) also lies relatively close to the transition line between the 50% and 100% coverage, and it is possible that small perturbations (maybe related to the cluster shape) may determine the edge configuration of the clusters. An image of this situation is illustrated in Fig. 7.9(b) where two clusters (one triangle, and one truncated
7.4 Approaching HDS conditions: \textit{ab initio} thermodynamics

Figure 7.9: (a) Re-sulfidation: Atom-resolved STM image of a hexagon-shaped MoS$_2$ nanocluster resulfded at 573 K in $1 \times 10^{-6}$ mbar of H$_2$S. The Mo edges (long) now show protrusions, with characteristics of the S dimers (double period etc.). (b) Intermediate synthesis conditions: An atom-resolved STM image illustrating two clusters with differently terminated Mo edges (see legends). The STM scan direction is indicated with an arrow.

hexagon) are each found to exhibit different edge stoichiometries. Both the dimers and the monomers are seen to exist within the same cluster (the hexagon). The monomer-terminated edge is identified by the characteristic low intensity of the outermost row. The STM image was scanned horizontally line-by-line, and the fact that two edges with the same orientation on the substrate are imaged differently excludes tip artifacts as the origin of the effect. These observations supports the conclusions in Section 5.2, where it was suggested that the edges exhibiting S vacancies are Mo edges with monomers, whereas the other edges terminated by dimers exist as well under the same conditions. It is furthermore interesting to notice that the smaller triangular cluster in Fig. 7.9 is exclusively terminated with S dimers, even at these intermediate conditions. As the figure suggests, this does not exclude the possibility of having other clusters terminated by monomers under the same conditions, but rather confirms that corner energies associated with the triangles have a very strong impact on the morphology and equilibrium edge terminations.

Returning to the phase diagram of the Mo edge in Fig. 7.8 a point is plotted corresponding to realistic HDS conditions. At the high temperatures and high pressure of H$_2$, the chemical potential of hydrogen is high and the corresponding chemical potential of sulfur is low. The point is illustrated in the phase diagram with the open circle denoted (HDS). The position of this point lies in the stability region where the Mo edge maintains a half S coverage, i.e. S monomers, but the much higher chemical potential of H additionally opens up for the possibility of stable H species adsorbed on the Mo monomers. Hence, when the results are in this way extended to realistic HDS conditions in the thermodynamic model, the S coverage is the same on the Mo edge as in the STM findings. It was not possible to address the adsorption of hydrogen on the monomer-terminated Mo edges in this study, since the chemical potential of hydrogen was apparently too low. The configuration which is predicted in the thermodynamical model has hydrogen adsorbed on every second monomer S on the Mo edge, and the adsorption energy of H is $\Delta E_{H} = -0.30$ eV [104, 174].

One can, however, speculate on the significance of this in relation to the reactivity of
the edges and in particular with reference to the mechanism suggested in Chapter 6.3 for the hydrogenation of thiophene. Evidently, reactive hydrogen will be abundant on the Mo edges during real hydrotreating conditions, and may thus enter the reaction with thiophene adsorbed on the bright brim. This of course requires that the bright brim associated with an edge state on the reduced Mo edge also has favorable adsorption sites. Experiments are planned which will investigate this further, and possibly confirm that the reaction path demonstrated for thiophene may be of general importance also at realistic HDS conditions.

In conclusion, a thermodynamical treatment of the Mo edge of MoS$_2$ confirms the main findings based on STM. Under sulfiding conditions the Mo edges are fully saturated with S dimers, whereas the preferential type of edge-coverage under reducing conditions is the half-saturated S monomer termination.

### 7.4.3 Thermodynamic stability of the S edge

The S edge of MoS$_2$ is found in the STM experiments to be exposed only under reducing conditions. Under these conditions, atom-resolved STM images reveal that the S edges of the hexagon-shaped MoS$_2$ triangles (Fig. 7.4) are fully saturated with S and maintain a coverage of H species adsorbed on the edge sulfur atoms (Fig. 7.7).

In the phase diagram, points are plotted with the extremes corresponding to the chemical potentials during synthesis, Red(1), and during the subsequent STM imaging, Red(2). Here, the two points are situated in different stability regions implying the possibility of a phase transition. During synthesis, the thermodynamically stable stoichiometry of the S edge is found to have a 75% S coverage, i.e. with every second S atom from the dimers removed\(^3\). At imaging conditions the point has moved to the stability region of the fully sulfur covered S edge with H adsorbed. If thermodynamical equilibrium is achieved, the point Red(1) represents the situation during synthesis, and it appears from the STM findings that a phase transition occurs as imaging conditions are approached.

Apparently, the transition between the two stability regions is non-activated, unlike on the Mo edge, and it occurs before the clusters are imaged with STM. This absence of an activation barrier may be explained by the less complicated structural rearrangements associated with the transition from the S edge with 75% coverage to the observed situation, which primarily only involves adsorption of S on a vacancy site. This may occur by S adsorption when UHV conditions are achieved after the synthesis. Hence, if the adsorption of S is not kinetically hindered, the theoretical calculations are in agreement with the experimental situation.

More importantly, the thermodynamic model predicts that the edge configuration observed with STM also corresponds to the stable configuration under real catalytic process conditions (point HDS in Fig. 7.8), and it is suggested that the S edge configuration observed with STM is identical to the S edges under real catalytic conditions. Hence, the state of the catalyst model system, consisting of single-layer MoS$_2$ nanoclusters synthesized under reducing conditions, corresponds quite well to what is expected of MoS$_2$ under realistic

\(^3\)Although a 75% sulfur coverage implies the formation vacancies on every second site on the edge it is misleading to associate these with active sites for HDS since the calculations are performed in thermodynamical equilibrium. Active sites in the form of single vacancies are believed to form dynamically by small local fluctuations away from the equilibrium coverage of S.
HDS operating conditions.

The S edge gains a large amount of energy by adsorbing hydrogen, $\Delta E_H = -1.26\text{eV}$. This has important consequences in relation to the reactivity of this type of edge, and especially the formation of sulfur vacancies. The tendency to form vacancies on the S edge is tested in the STM experiments by exposing the clusters to further hydrogen. In the studies no indication is seen that such vacancies are formed on the S edge even by the rather large exposures of hydrogen in this study. Nor does exposure to highly reactive atomic hydrogen result in the formation of vacancies under the conditions of our experiments, and it is concluded that the vacancy formation on the S edge is unfavorable.

To investigate why this is so, one can look at the energetics associated with vacancy formation. Starting from the fully sulfided S edge (i.e. without H adsorbed), several DFT calculations show that the energy required to remove one sulfur is much lower ($\Delta E_S \approx 0.2\text{ eV}$) [67, 104, 148] than for the same process on the Mo edge (e.g. $\Delta E_S \approx 0.6\text{ eV}$ for a vacancy on the monomer edge), and the vacancy formation would intuitively be expected to occur readily under the experimental conditions. However, if the starting point is the much more stable S edge with H adsorbed, the energetics are shifted correspondingly, and it is suggested that the hydrogen actually stabilizes sulfur on the S edges. Dosing large amounts of atomic hydrogen only increases $\mu_H$ and stabilizes the hydrogen adsorbed on the fully covered S edge even further according to the phase diagram in Fig. 7.8. This explains why vacancies are not observed in the STM experiments, since the S edges are already fully saturated with hydrogen under the conditions of the experiments. This also appears to be the case under real HDS conditions, and increasing the hydrogen pressure will consequently render the S edge less reactive.

Returning briefly to the issue of cluster morphology, the relatively large energy gain associated with the formation of S-H groups on the S edge may also explain the preferential hexagonal shapes of the MoS$_2$ clusters observed under reducing conditions. Under the sulfiding conditions of the previous chapters, the Mo edges were found to be energetically more stable than the S edge by a factor of two. This was inferred from the predominantly triangular equilibrium shape. When the chemical potential of H is increased in the present study, hydrogen adsorption is favored on the S edges thereby effectively shifting the edge free energy of the S edge relative to the Mo edge. The predominantly hexagonal shape is a reflection of the fact that the Mo edge and the S edge now have comparable edge free energies, i.e. with a ratio below 2. (see Fig. 4.3). The exact magnitude of the ratio of the edge free energies can be extracted by consideration of the shapes of the MoS$_2$ clusters. This analysis will be performed in the next section.

Before doing so, a comment is warranted concerning a recent study by Schweiger et al. In this DFT-based study, the difficulty of extracting absolute values of the edge free energies of the Mo edge and S edges independently was solved by elaborate calculations employing a supercell containing triangular MoS$_2$ clusters exposing one or the other type of edges [105]. In this way it was possible to compare directly the edge free energies and thus investigate the morphology of the clusters under various environmental conditions in terms of a similar thermodynamic model as outlined above. In accordance with the STM results in the previous sections, the shape of a single-layer MoS$_2$ nanocluster is predicted to be a triangle under sulfiding conditions. As more reducing conditions are approached, the S edge is found to gain in stability and the equilibrium size is then predicted to be a corner truncated triangle.
The cluster calculations do, however, not include the possibility of adsorbing hydrogen on edge sites via reaction 5.3 and consequently do not predict the rather large stabilizing factor of the H on the S-edge. This has consequences for the predicted equilibrium shape of the MoS$_2$ nanoclusters. Following the trend of the cluster calculations, the shape is thus expected to be significantly more truncated under reaction conditions, possibly approaching an almost perfect hexagonal shape or even with the S edge dominating. Throughout this thesis, the importance of finite size effects has also been emphasized, partly in terms of the S coverages of smaller clusters, but also through their shape, which appears to be size dependent. Such corner effects only enter in the cluster calculations partly, and must be included fully in order to account for the morphology observed with STM.

7.5 Morphological impact of hydrogen

In order to shed further light on the morphology of the hexagon-shaped MoS$_2$ nanoclusters synthesized in a hydrogen ambient, the size-dependence of the cluster shape is investigated in this section. For this purpose, the morphology is now investigated at three different temperatures, i.e. the MoS$_2$ nanoclusters are synthesized under reducing conditions (7% H$_2$S) at 673 K, 723 K and 773 K, respectively. For all experiments the annealing time was fixed at 15 minutes (see Fig. 3.3).

The main effect of increasing the postannealing temperature during synthesis is the activation of an enhanced agglomeration and bigger, but still single-layer MoS$_2$ clusters thus form. It will become evident from the following that this increase in cluster size also affects the shape of the clusters. When postannealing to 673 K, 723 K and 773 K, the average cluster size increases gradually from $\sim 450$ Å$^2$ to $\sim 650$ Å$^2$ and $\sim 900$ Å$^2$, respectively. This is in accordance with the results in Section 4.9 for the fully sulfided structures. It is, however, emphasized that under sulfiding conditions, the equilibrium shape is the triangle irrespective of cluster size (see Section 4.9). The clusters synthesized under reducing conditions behave quite differently. At the three temperatures lower than 773 K, a predominant shape of more or less truncated hexagons could be defined. At substrate temperatures above 773 K, the conclusions from a shape analysis become too obscured by the agglomeration effects, and are not suitable for these experiments. However, like in Section 3.4, the initial disorder and the occurrence of metastable structures can be reversed by increasing the annealing duration.

The shape of the clusters synthesized under reducing conditions is shown in Fig. 7.10(a) as a function of the size. Each point in the graph corresponds to a single cluster. The shape of the clusters is represented by a single parameter – the ratio of edge free energies $\gamma_S/\gamma_{Mo}$, which was derived for each cluster from the geometrical construction exemplified in Fig. 7.10(b). Preferably, such an analysis should be performed on atom-resolved images, but the number of suitable images from each preparation was far too low to get sufficient statistics. Hence, the analysis relies on overview images (typically 500×500 Å$^2$), where the detailed characterization is hampered by limited resolution and tip broadening effects, which introduce large scattering on the values characterizing the shape. The data, however, reveal a clear trend indicated with a guiding line.

Judging from the trend in Fig. 7.10(a), the clusters seem to adopt a more hexagonal
shape as the clusters increase in size, whereas the smaller clusters appear more triangular ($\gamma_S/\gamma_{\text{Mo}}$ approaching 2). For the biggest clusters synthesized here the ratio of edge energies levels off and can be roughly estimated by inspection of Fig. 7.10 as:

$$\frac{\gamma_S}{\gamma_{\text{Mo}}} = 1.35 \pm 0.25$$

(7.7)

i.e. corresponding to clusters which adopt a hexagonally truncated shape. The S edges and Mo edges are readily distinguishable in atomically resolved STM images of the clusters, and on the basis of a considerable number of such images it is concluded that the Mo edges dominate over the S edges in the hexagon-shaped MoS$_2$ clusters. From geometrical considerations and the estimated value of $\gamma_S/\gamma_{\text{Mo}}$ it is therefore concluded that between 10-30% of the edge sites pertain to the S-edge and 70-90% to the more stable Mo edge in a hexagon-shaped MoS$_2$ cluster under the present conditions.

It is noticed that the smallest clusters (below $\sim$ 500 Å$^2$), still prefer a more triangular shape, even synthesized under the present reducing conditions. This observation is attributed to their smaller size. It is suggested that the preferred triangular shape of the smaller clusters in the present case is the result of finite size effects related to the corners, since these will have a larger impact for the smaller sizes. This also provides an explanation why a clear contrast between shapes synthesized under sulfiding and reducing conditions is not observed at 673 K, whereas a clear trend is observed at 723 K and 773 K. At 673 K the average size of the clusters is approximately 450 Å$^2$, and, hence, the majority of the clusters have sizes where the shape seems to be dominated by their finite size irrespective of the gas composition. This is not as pronounced when postannealing to higher temperatures, since the average cluster size then increases correspondingly. The fact that smaller clusters are less affected by the hydrogen ambient is also in accordance with the STM findings in
e.g. Chapter 5, where even rather large exposures of atomic hydrogen at temperatures up to 673 K change little with respect to morphology (but significantly in terms of edge structure, i.e. vacancies and S-H groups).

In order to make the graph in Fig. 7.10(a) converge and achieve the true Wulff shape of the clusters, even larger structures have to be investigated. The discussion is, however, somewhat academic from a catalytical point of view, since the corner effects in the smaller structures by the above considerations, will most likely play a role in the real catalyst as well. It is therefore concluded that predominantly larger MoS$_2$ clusters approach a more hexagonal shape when synthesized under reducing conditions.

### 7.6 Conclusions

This section reports on new and interesting insight into the morphology and edge structures of single-layer MoS$_2$ nanoclusters synthesized in a gas composition which resembles the mixtures used for HDS under working conditions. MoS$_2$ clusters are found to adopt preferentially a hexagonal shape as opposed to the triangular shape under sulfiding conditions. In atom-resolved STM images the nature of the two fundamentally different edges terminating the hexagonal clusters is unravelled. Under the conditions of the experiment, the Mo edges maintain a half-saturated coverage with S monomers. The S edges are fully saturated with sulfur, and hydrogen is furthermore found to adsorb on the edge to form S-H groups. These findings are corroborated in terms of DFT calculations and a thermodynamical model extending the zero-pressure, zero-temperature theoretical results to the experimental conditions. When extrapolating the results to working HDS conditions it is shown that the experimentally observed state of MoS$_2$ clusters does not differ much from the predicted edge stoichiometries in the catalyst. The model system of single-layer hexagon-shaped MoS$_2$ nanoclusters thus represents a well-characterized reference for future experiments addressing important issues of the cluster reactivity. Experiments performed by dosing thiophene as a test-molecule are planned in future work, and maybe this will reveal further atomic scale insight into the mechanisms of the hydrodesulfurization. So far, the effect of the high pressures (> 10 bar) during real catalytic conditions has been neglected, and it is difficult to predict from the present studies which kind of effect it will have on the morphology. One way of addressing this kind of issue would be to synthesize the clusters in a high-pressure cell attached to the UHV chamber. Furthermore, a high-pressure STM capable of atomically resolving single-crystal surfaces is available in the STM-laboratories at the University of Aarhus [9,202], and by *in situ* monitoring of the present model system new and essential insight may be achieved.
Chapter 8

The Atomic-scale Structure of CoMoS Nanoclusters

The hydrodesulfurization activity of the cobalt-promoted catalyst is typically more than an order of magnitude higher compared to unpromoted MoS$_2$, and in previous studies exploring structure-activity relationships, this enhanced activity has been shown to correlate uniquely with the formation of bimetallic sulfided Co-Mo structures, termed CoMoS [52]. These are characterized as MoS$_2$-like nanoclusters with Mo substituted by Co at edge sites. However, the origin of the promoting role of Co and, in particular, the atomic-scale location of the promoter atoms in CoMoS is still the subject of intense debate. This is related to the fact that the traditional spectroscopic techniques, which provide insight into the nature of CoMoS, are not able to unequivocally map the real-space atomic structure.

In this chapter the catalyst model system consisting of gold-supported MoS$_2$ nanoclusters will be extended to include the effect of Co promoters. The aim is to optimize the conditions under which Co and Mo mix to form the bimetallic CoMoS phase in the model system, and to study the synthesized structures with STM in terms of their morphology, atomic-scale structure and reactivity.

8.1 Preparation of CoMoS nanoclusters

The tendency to form the bimetallic sulfide phase on the Au(111) substrate is found to be influenced much by the exact choice of preparation procedure. This is not surprising since changes in preparation parameters of the industrial catalysts also strongly influence the phase distribution. In particular, phase separation of the Co and Mo is seen to be pronounced and must be prevented to ensure a high performance of the Co-promoted catalyst. The preparation procedure, which will be described below, is found to be particular efficient in the synthesis of the bimetallic CoMoS.

The starting point is again the standard preparation of MoS$_2$ nanoclusters (Section 3.3). This serves as a well-characterized reference, and any observed changes in the surface structure can be traced back to the effect of Co. Like Mo, Co is found to belong to the class
The Atomic-scale Structure of CoMoS Nanoclusters

of materials that nucleate in the “herringbone” elbows of the Au(111) surface reconstruction [129, 134, 203], i.e. Co deposited from the e-beam evaporator source can be dispersed into nanoclusters in a similar fashion (See e.g. Fig. 8.8).

The idea behind the synthesis of CoMoS is to form embryos of molybdenum sulfide followed by capping of these nanoclusters with Co to facilitate the addition of Co to the edges of MoS$_2$ nanocrystals. Initially, a core of sulfided Mo is produced by e-beam evaporating Mo onto the clean Au(111) substrate while dosing gaseous H$_2$S at a rate corresponding to a chamber pressure of 1 × 10$^{-6}$ mbar. Following the initial deposition of pure Mo (8 minutes, 1.7 × 10$^{-4}$ ML/sec), Co and Mo are subsequently co-deposited (2 minutes, both 1.7 × 10$^{-4}$ ML/sec) to provide an intermixed capping of the initial nanoclusters located on the reconstructed Au(111) template while maintaining the flux of H$_2$S molecules. Prior to the synthesis, the individual quantities of the Mo and Co were estimated in STM images from the density of nanoclusters on the Au(111) and found to be 2 ± 1% for Co and 10 ± 1% for Mo, yielding a Co/Mo ratio which resembles that of the optimum Co promoted catalyst [29]. In the final step of the synthesis, the clusters are crystallized by postannealing the sample at 673 K for 15 minutes while keeping the H$_2$S background pressure. Further experimental details of the synthesis are given in Section 3.1.

8.2 Characterization of CoMoS nanoclusters

The co-deposition of Mo and Co in an H$_2$S atmosphere is seen from STM images to result in the synthesis of two significantly different co-existing structures: (i) large cobalt-sulfide islands formed by step-flow growth (Fig. 8.1a,b) and (ii) crystalline CoMoS clusters nucleated on the Au(111) terraces in Fig. 8.1(c). In Fig. 8.1(a,b) a large island nucleated at a Au(111) step edge is seen together with an atom-resolved image of the characteristic structure. These rather large islands are associated with the formation of a cobalt sulfide, since similar structures are observed when only Co is deposited and subsequently sulfided on Au(111) (Section 8.8). Cobalt sulfide is known to exist in a variety of phases with different stoichiometries and crystallographic structures, e.g. Co$_8$S$_9$, Co$_3$S$_4$ or CoS$_2$ [204], but in view of their low catalytic significance and apparent complexity, a thorough analysis of their detailed structure in the STM images has not been performed. In this context, it is, however, worth mentioning that Co$_8$S$_9$ is the thermodynamically most stable cobalt sulfide and is present in heavily promoted Co-Mo sulfide catalysts under operating conditions (Fig. 1.7) [29, 52].

The following discussion will thus be concerned with the sulfided crystalline CoMo structures nucleated on the Au(111) terraces (Fig. 8.1c). One of the main new findings is that the crystalline nanoclusters synthesized under fully sulfiding conditions have a predominantly hexagonal shape as opposed to the triangular morphology of unpromoted MoS$_2$ (Fig. 3.4) observed when only Mo was deposited and sulfided. The majority of the clusters (> 80%) are found to be crystalline with the rest either being too small to be characterized or without a clear structure. Of these more than 70% have the shape of a truncated hexagon\(^1\), suggesting that this is the equilibrium shape of the clusters. This change in the equilibrium

\(^1\)A truncated shape refers to the fact that clusters synthesized without Co are triangular, i.e. the hexagons are considered as corner truncated triangles.
Figure 8.1: Panel of STM images showing the surface structures formed upon sulfiding Co-Mo on the Au(111) surface at 673 K. (a) STM image (152×186 Å$^2$) of large cobalt sulfide islands at the Au(111) step edges. The cobalt sulfide islands range in width from 100 to 500 Å. The smaller embedded structures are attributed to encapsulated MoS$_2$ islands. (b) STM image (50×54 Å$^2$) showing atomic resolution on part of a cobalt sulfide island. (c) Large-scale image (630×644 Å$^2$) showing the morphology of the single-layer CoMoS clusters nucleated on the Au(111) terraces. The predominant shape is found to be hexagonal.

Shape is therefore attributed to the incorporation of cobalt into the MoS$_2$ structure, i.e. the formation of the CoMoS phase. Before proceeding, it is worth noticing that the effect of the Co promoters on the morphology on the MoS$_2$ nanoclusters appears to be similar to that observed in case of exposing the cluster to a reducing atmosphere during synthesis in Chapter 7. The present experiments are, however, performed under fully sulfiding conditions and the observed morphological effect is in this case not induced by hydrogen but rather the incorporation of Co into the edge structure of the cluster. This is also reflected in the tendency of even the smallest CoMoS clusters to adopt a hexagonal structure whereas the smallest unpromoted MoS$_2$ clusters (< 450 Å$^2$) prefer a triangular shape irrespective of the gas compositions used for the synthesis.

Atomically resolved STM images of the hexagonally shaped nanoclusters (Fig. 8.2) reveal a basal plane of hexagonally arranged protrusions with an interatomic spacing of 3.15 ± 0.10 Å. This is in exact agreement with the value of the (0001) basal plane of MoS$_2$. The height profile of the clusters also corresponds to the values found for the single-layer MoS$_2$ nanoclusters in previous chapters (see e.g. Section 4.1). It is therefore concluded that the internal structure of the CoMoS clusters coincides with that of single-layer MoS$_2$. 
nanoclusters, i.e. the clusters are indeed “MoS$_2$-like”. The impact of Co promoters is thus primarily seen to be concerned with the edges of the clusters, in full accordance with the CoMoS model.

### 8.3 CoMoS edge structure

The predominant hexagonal morphology implies that both fundamental types of low-indexed edge terminations of MoS$_2$ must be present, i.e. the Mo edge and the S edge. The identity of the two types of edges in CoMoS is inferred from atom-resolved STM images (Fig. 8.2). In the truncated hexagonal clusters, one edge-type is found to be similar to that observed for the MoS$_2$ triangles (Fig. 4.1), with the edge protrusions clearly imaged out of registry with the lattice of S atoms on the basal plane and a bright brim along the edge with a height of $0.3 \pm 0.1$ Å above the basal plane. These edges are therefore identified as Mo edges, fully sulfided with two S dimers per Mo edge atom (see Fig. 8.3b). Hence, Co promoter atoms appear to have little effect on the Mo edges.

From the symmetry of MoS$_2$, the other, shorter edges are consequently attributed to S-type edges. The results suggest that Co promoter atoms stabilize these new types of edges and, consequently, that the morphological transition observed with STM is driven by this preference for Co to be located only at the S edges. The features of the S edge are depicted in the atom-resolved STM image (Fig. 8.2). A grid superimposed on the basal plane S atoms, reveals that edge protrusions are imaged close to positions in registry. Compared to the position of the bulk lattice, however, a slight displacement of $\sim 0.5$ Å perpendicularly away from the edge is observed. The edges also exhibit a very bright brim extending along the edge in the row immediately behind the edge protrusions. Clearly, this edge has similarities with the unpromoted S edge in the hexagonal MoS$_2$ structures synthesized in a reducing atmosphere (Chapter 7). This immediately suggests the existence of one or more metallic edge states. The brim structure is, however, imaged significantly brighter, with a height of $0.9 \pm 0.2$ Å above the basal plane atoms. It is suggested that this change in the LDOS is associated with the presence of Co atoms at the S edge. Cobalt edge atoms appear to donate further electron state density to the surrounding S atoms which consequently are imaged more brightly. It is possible that the perturbed electronic environment of the sulfur atoms neighboring the Co atoms may be a key to understanding the increased reactivity of the CoMoS structures.

### 8.4 New structural model for CoMoS

On the basis of the detailed atomic-scale information provided by the STM images, a structural model of the CoMoS nanoclusters is proposed in which Co atoms have substituted Mo atoms along the S edges of hexagonally truncated nanoclusters. As depicted in the ball model in Fig. 8.3(a) and (c), a tetrahedral environment of the Co atoms is produced if the outermost protrusions are assumed to be S monomers. The proposed CoMoS model is thus seen to have intrinsic under-coordinated sites at the S edge, and from a catalytic perspective this may be an attractive situation enabling adsorption of sulfur containing reactants.
Figure 8.2: (a) Atom-resolved STM image of a CoMoS nanocluster. Size $51 \times 52 \text{ Å}^2$ and $V_t = 95.2 \text{ mV}, I_t = 0.81 \text{ nA}$. Notice the very intense brim associated with the Co-substituted S edge (shorter edges).
The presence of bridge-bonded monomer atoms located in-plane with the metal lattice of the S–Mo–S structure is consistent with the apparent outwards displacement of 0.5 Å as observed with STM in the clusters. The possibility of Co having only substituted a fraction of the Mo atoms at the S edge seems unlikely. At no instance were CoMoS clusters imaged with a periodicity larger than one lattice constant along the S edge, indicating a complete substitution with Co along the edges.

The present model for CoMoS agrees well with previously published spectroscopic results on supported CoMoS catalysts. From in situ EXAFS [41, 46, 205, 206] measurements, the local environment of substituted Co atoms has been inferred, and it is shown that the average distances from Co to the nearest atoms are $d_{Co-S} \approx 2.2$ Å and $d_{Co-Mo} \approx 2.9$ Å. Furthermore, the average coordination was found to be $N_{Co-S} = 5 \pm 1$ and $N_{Co-Mo} \approx 2$. These coordination numbers are consistent with the fully substituted S edge model shown in Fig. 8.3. Although the present interpretation of the STM observations may be supported by STM simulations of the edge structure, it is noteworthy, that previous DFT studies show
8.5 **Morphology of CoMoS**

The main morphological impact of Co on the MoS$_2$ based clusters is to change the shape of the single-layer cluster from triangular to hexagonally truncated. Neither the stacking nor the orientation of the clusters on the substrate seem to be affected. The shape of the CoMoS clusters is determined by a preference for Co to be located on the S edges only, and within the concept of the Wulff construction the morphological influence may be explained by a stabilization of the S edge by Co substitution relative to the Mo edges, thus effectively causing the cluster to expose both types of edges. Evidently, the actual shape of each cluster is dependent on a number of factors, such as the total amount of Co substituted on the edges and possible finite size effects on the Mo edges (even/uneven number of dimers). Consequently, the CoMoS clusters formed in present synthesis cannot be characterized with a unique shape, unlike their unpromoted counterparts exhibiting a triangular shape only. A detailed shape analysis of the truncated CoMoS clusters reveals that the degree of cluster truncation varies with edge free energy ratios $\gamma_S/\gamma_M$\textsuperscript{2} in the range 1.1 to 1.6, i.e. from almost perfect hexagons to slightly truncated triangles with Mo edges dominating. No particular correlation between these values and the cluster size is found.

Furthermore, with respect to size, the CoMoS clusters are generally larger than their unpromoted counterparts synthesized at the same conditions (450 Å$^2 \pm 200$ Å$^2$ at 673 K, Section 3.4). With only a slight increase in the total coverage of the surface structures, a size distribution reveals that the average size of CoMoS clusters crystallized at 673 K is 700 Å$^2$ and increases to 850 Å$^2$ as the postannealing temperature is raised to 723 K. For

\textsuperscript{2}The ratio of edge free energies was derived in a similar way from the Wulff construction as demonstrated in Section 3.4 and Fig. 7.10.
both preparations, the cluster size distribution also appears less narrow than for MoS$_2$, with standard deviations of 350 Å$^2$ and 400 Å$^2$, respectively. Variations with temperature are again attributed to enhanced surface mobility.

The apparent scattering of shapes is suggested primarily to be caused by local variations in the Co coverage available during nucleation of the CoMoS clusters. The truncated hexagonal shape is the equilibrium shape of CoMoS, but due to the strong perturbing effect by even rather small amounts of Co present at the edge, the morphology of the clusters is extremely sensitive to the total amount of Co present during synthesis. As will be become evident in Section 8.8, Co species are very mobile on the Au surface in the presence of H$_2$S even a room temperature, and it is possible that a redistribution of Co occurs rapidly during synthesis causing the Co content to vary between individual clusters and thereby the shape to fluctuate around the equilibrium form. However, increasing the Co coverage further in an attempt to reach saturation did not lead to a higher content of Co in the clusters, nor did it increase the homogeneity of the cluster shapes. It merely facilitated the formation of additional cobalt sulfide capping the clusters – a scenario also recognized from real promoted catalysts, where heavy Co promotion is followed by a decrease in activity due to Co$_8$S$_8$ production, which is inactive in HDS. Hence, it is concluded that the cluster morphology is sensitive to the promoter content and that the present procedure seems to be the most optimum way of synthesizing gold-supported CoMoS clusters.

The less homogeneous appearance of the promoted CoMoS clusters can also partly be explained by the absence of finite size effects affecting the size and shape. Evidence of this is provided by atom-resolved images of the CoMoS clusters, e.g. the two clusters illustrated in (Fig. 8.4). Both of these clusters are synthesized under the conditions quoted in Section 8.1 and have a similar size. On some of the (longer) Mo edges in these two clusters, it is interesting to notice that the constraint concerned with only even numbers of S dimers has been lifted and now edges terminated by an odd number of S dimers (i.e. an even num-
ber of protrusions) also occur, which do not exhibit the double period. In Section 4.7, the preference for the unpromoted MoS$_2$ clusters to assemble with a triangular shape and with a quantized size was explained in terms of this double period, since it is associated with an energetically favorable pairing of the S dimers. This leaves a terminal S dimer unpaired in edges with an odd number of S dimers, which consequently do not form at all. For the CoMoS clusters, the energy gain associated with the pairing of S dimers seems to be lifted in structures with an odd number of edge S dimers. Only edges which (occasionally) are terminated by even number of S dimers display the double period, and it is therefore concluded that the perturbing effect of Co entering the S edges must be relatively somewhat stronger than the finite-size effects dominating the unpromoted triangular structures.

The fact that the clusters exhibit shapes with varying degree of truncation, suggests that the growth of CoMoS clusters is not limited in the same way as the MoS$_2$ triangles, to the growth mode of which only permits an even number od S dimers. The CoMoS clusters can grow with an arbitrary amount of Mo only limited by normal kinetic effects of ripening and the amount of Mo and Co locally present for the synthesis, and the morphology thus becomes less homogeneous in the experiment. The less constricted growth of CoMoS compared to MoS$_2$ synthesized under the same conditions also agrees well with the fact that the rather large increase in average cluster size can not be explained alone by the incorporation of Co in the vicinity of the S edges, which geometrically only represents a rather low portion of the cluster area.

8.6 Reactivity of CoMoS – Promotional effect of Co

In the literature, the promotional effect of Co has been proposed to be due to a weakening of the sulfur bond strength in the CoMoS structure [64, 70] and, hence, a corresponding increase in the number of S vacancies at the edges. The STM results demonstrated above show directly that the electronic structure and, presumably, also the bonding strength of the neighboring S atoms is influenced by the presence of Co. The geometrical model based on the STM results predicts that sulfur monomers are maintained on the Co-promoted edges, i.e. they are intrinsically under-coordinated. However, since the clusters are synthesized under sulfiding conditions, and this is the S saturated structure, it is therefore doubtful whether S containing reactants will adsorb readily here. The tendency of the Co-substituted S edge to react further and form vacancies is therefore experimentally investigated by exposing the promoted model system to hydrogen and subsequent imaging with STM. Furthermore, the affinity of the Co-promoted structures to adsorb and react with thiophene is investigated.

8.6.1 Hydrogen adsorption on CoMoS

Exposing the clusters to hydrogen – atomic or molecular – leaves the edge structure of the Co-substituted S edge unaltered in STM images. No signs of vacancies or changes due to the formation of S-H groups are observed by dosing hydrogen in rather large exposures (< 1100 L). This could, in principle, be related to a rather large energy associated with the formation of vacancies in the row of S monomers, but taking into account the large dosage of highly reactive atomic hydrogen atoms, a different explanation is more likely: It
is tentatively suggested that hydrogen atoms are already fully covering the sulfur atoms on the Co-saturated edge and form S-H groups. If hydrogen adsorbs in a stable configuration on the Co-substituted S edge, exposing it to hydrogen just drives the reaction for S-H formation further and consequently no (or extremely few) vacancies are formed under the conditions of the experiment. A similar scenario was presented for the unpromoted S edge (Section 7.4.3), and here S-H groups were indeed found to influence the formation of vacancies.

It is suggested that even the small amounts of hydrogen present during synthesis due to decomposition of H₂S are enough to create full coverage of hydrogen on the Co-substituted S edge, i.e. through a reaction:

\[ \frac{1}{2} H_2(g) + (S_{Co} - \square) \rightleftharpoons S_{Co} - H_{ads} \]  

where \( S_{Co} - \square \) denotes a sulfur atom on the promoted edges with an empty adsorption site for hydrogen. The amount of adsorbed hydrogen depends on the actual S coverage, but with reference to the proposed configuration in Fig. 8.3(c), it is tentatively suggested that one H adsorbs on each edge sulfur. This is an elaboration of the model proposed in the previous section and the modified Co-promoted S edge is depicted in Fig. 8.3(d).

The chemistry of the dimer-covered (unpromoted) Mo edges (Fig. 8.3b) towards hydrogen was mapped for the single-layer triangular MoS₂ cluster in Chapter 5. Although, the CoMoS clusters exhibit these types of edges too and Co has no immediate effect on the edge structure, the chemistry is still expected to be slightly different, since the edges are not dominated to the same extent by the stabilizing finite-size effects associated with the double period and paring of S dimers. Following the hypothesis presented for the vacancy formation on the triangular structures in Section 5.2, it should thus, in the absence of stabilizing finite-size effects, be much easier to reduce the clusters with hydrogen to form monomer-terminated Mo edges or even vacancies, at least on edges with an odd number of S dimers. Preliminary experiments show that the dimers on the Mo edges can be reduced with molecular hydrogen (H₂). This is illustrated in the STM image in Fig. 8.5 where the sample of CoMoS clusters was exposed to molecular hydrogen at 600 K. Here, the Co-promoted S edges appear unaltered by the hydrogen treatment, whereas the three Mo edges are imaged with a very low intensity on the outermost protrusions. Exactly this is a predominant characteristic of the Mo edge with monomers (Section 7.3.1), and it is therefore concluded that the Mo edges can be readily reduced to monomers in the CoMoS clusters on Mo edges which are not initially stabilized by finite-size effects. A similar effect is expected to exist in the unpromoted MoS₂ hexagons (Chapter 7), but since the initial state of the Mo edges of these is already reduced to the half-saturated coverage, this was not investigated in the present studies. Concerning the CoMoS clusters, further experiments need to be performed at this stage to establish if additional treatments with atomic hydrogen will facilitate the formation of a significant number of vacancies on the monomer-terminated Mo edges like for the triangular clusters (Section 5.2), and in that case, if the vacancy formation occurs more readily.

The present STM findings on the Co-substituted S edges may be supported by future DFT calculations on the promoted structures along the same line as the results in Chapter 7. At present, no detailed DFT calculations have confirmed the existence of H on the fully Co-substituted S edge which is found here, but a preference for H to adsorb on a similar
configuration has previously been investigated. Byskov et al. found the adsorption of hydrogen to be favorable on an S edge with every second Mo substituted by Co and terminated with S dimers [67]. It is noted that similar intrinsic under-coordinated sites associated with the S monomers were also found near the Co atoms in the theoretical studies. It would be interesting to extend the low pressure results to working conditions in terms of a thermodynamic model. Such calculations may also provide information on the existence of any metallic one-dimensional edge states at the Co-substituted edges.

The high intensity of the brim structures observed with STM clearly suggests that metallic edge states are available on this edge. Their existence is a highly interesting aspect in relation to the promoting role of Co, since similar one-dimensional metallic states on the Mo edges were found to have a remarkable kind of chemistry, i.e. being able to adsorb and dissociate thiophene in the presence of hydrogen. The interaction of thiophene (\( \text{C}_4\text{H}_4\text{S} \)) with the Co promoted edges is the subject of the next section. For now, it is concluded that hydrogen exposures under the present reaction conditions do not facilitate the formation of sulfur vacancies on the promoted edges due to a competition with adsorbing hydrogen, which binds in the energetically most favorable situation.

### 8.6.2 Thiophene adsorption on CoMoS

To test the affinity of the promoted clusters towards adsorption of S-containing reactants, experiments were conducted with thiophene (\( \text{C}_4\text{H}_4\text{S} \)) as a test molecule. The procedure
follows the experimental details listed in Section 6.1. Experiments were carried out by exposing the freshly prepared model system of CoMoS clusters to thiophene dosed from the gas-phase at temperatures in the interval from 200 K up to 500 K, followed by mapping of the resulting structures with STM.

Direct exposure of thiophene at temperatures in the interval from room temperature up to 500 K onto CoMoS reveals significant changes of the clusters in atom-resolved STM images. The freshly prepared CoMoS clusters are found readily to facilitate the adsorption of molecules onto sites on the Co-promoted S edges. This is displayed in Fig 8.6. Here, a general increase in the average level of the bright brim above the basal plane is seen from \( \sim 0.9 \) Å (Fig. 8.2) to more than \( \sim 1.3 \) Å (maximum values). This is not an electronic effect of the brim, but is rather associated with adsorption of individual thiophene molecules on top of the protrusion of the Co-promoted S edge. Although the STM image does not reveal intramolecular resolution, the position of the molecules associated with the significantly higher protrusions must be in registry with the basal plane, i.e. a direct interaction with the underlying S atoms associated with the bright brim of the Co promoted edges. It is corroborated by the fact that the lateral extension of the brim protrusions is also increased compared to the clean edge, i.e. from approximately 2.0 Å to 3.0 Å characterized by the full-width-at-half-maximum (FWHM) values in the line scans Fig. 8.6(b). Concerning the identity of the adsorbed molecules, it was not possible to achieve intramolecular resolution, but it is speculated that the adsorbed species are either intact thiophene molecules or hydrogenated derivatives, e.g. 2,3-dihydrothiophene \((C_4H_6S)\) coordinated with the \( \pi \) electron
system in parallel to the cluster.

Additionally, two distinct types of structures are on the bright brim. These features are illustrated by the line scans in Fig. 8.6(b) which compared the thiophene reacted edge with an un-reacted Co-promoted S edge. (i) One type is associated with a clear extinction of the brim structure; (ii) the other is characterized by brim protrusions with exactly the same height (0.9 Å) as found on the edge without adsorbed molecules. Each of these can be associated with different reaction events on the Co-promoted S edge. The brim protrusions (i) which are in level with the non-reacted brim is simply an empty adsorption site. At the other type of sites (ii), the local disappearance of the brim suggests a disruption of the local electronic structure. It is proposed that this is caused by a hydrogenation reaction of thiophene with the pre-existing S-H groups on the Co edge. Upon removal of H atoms comprising the S-H groups, it is likely that the electronic (and maybe also geometric) structure changes locally, giving rise to the modifications in the STM images near the brim.

A similar reaction mechanism was presented for the reaction of thiophene on the Mo edge with S dimers, when it was pre-activated with hydrogen (Chapter 6.3). Here it was possible to correlate the signatures of species adsorbed on the brim in the STM images with thiophene molecules which had been sequentially hydrogenated and dissociated to form thiolates (see Fig. 6.6). A corresponding identification of the possible reaction path has not been performed in the present case yet, but the results clearly suggest a reaction occurring on the promoted edge.

The proposed hydrogenation reaction of thiophene seems to occur without a significant activation barrier on the promoted edges, since similar effects can be observed also when thiophene is dosed at low sample temperatures. The STM image in Fig. 8.7 shows a cluster exposed to thiophene at a temperature of 200 K, and even here the reaction signatures are observed on the brim, i.e. some protrusions on the brim appear reduced in intensity com-
pared to the immediate neighbors. Furthermore, at cryogenic temperatures weakly adsorbed thiophene molecules are also found to decorate the cluster perimeter (Fig. 8.7) in a similar fashion as for the unpromoted clusters (Fig. 6.2). Focusing on the shorter, promoted edges, individual thiophene molecules have snapped into contact and seem to be imaged with the aromatic ring system in parallel to the substrate. Hence, the nature of the interaction indeed appears to be different between the two types of edges, with the promoted edges more prone to interact with adsorbed thiophene.

In conclusion, the chemistry of the promoted CoMoS clusters demonstrated in this section points out certain trends which may explain the role of the Co promoter atoms. In particular, it is suggested that the Co-substituted S edges maintain a coverage of S monomers, and that this plays the role of an intrinsically under-coordinated edge which allows for an interaction with S containing molecules, either because it is less sterically hindered or due to the modified electronic structure. Furthermore, adsorbed S-H species may release hydrogen to enter a hydrogenation of unsaturated molecules like thiophene adsorbed on top of sites immediately behind the edges. Noticeably, the reaction occurs without an appreciable activation energy, and since such a hydrogenation of the aromatic structure is the first step towards complete hydrodesulfurization of thiophene due to the destabilization of the S heteroatom, this may partially explain the promoting role of the Co. It is noted that the proposed reaction again is an interplay between unusual adsorption sites near the bright brim on top of the cluster and hydrogen species adsorbed on the outermost S atoms.

Additionally, the Mo edges, which at first sight appear unaffected by the Co atoms in CoMoS clusters, are more easily reduced from the saturated edges (dimers) to edges covered with monomers than for the unpromoted counterparts. It was already argued that the Mo edges probably are the better starting point for the creation of edge sulfur vacancies in Chapter 5, and in this sense the clusters may thus have a higher coverage of S vacancies under working conditions. Altogether, the results confirm that the chemistry associated with hydrogenation and HDS seems to occur more readily on the promoted clusters compared to the unpromoted cluster, and that not only the local structural and electronic environment surrounding the Co atoms play a role but so do the properties of the entire cluster.

8.7 Conclusions on the CoMoS structure

The main result of the present chapter is the elucidation of the atomic-scale structure of CoMoS clusters. The study confirms the existence of the CoMoS phase, which has gained acceptance as the structural model for the promoted catalysts. A general method to synthesize the CoMoS is demonstrated. It is found that the particular hexagonally truncated morphology of the CoMoS clusters is driven by a preference for Co to be located only at the S edges, and that the Co content thus controls the shape of the cluster. On the basis of atom-resolved STM images a new model for the CoMoS phase is proposed which is consistent with previous spectroscopy data. Additionally, the electronic structure near the Co promoted edges is found in STM images to be significantly perturbed. Important aspects regarding the reaction with probe molecules (hydrogen, thiophene) are investigated, and certain trends related to the chemistry of the promoted clusters are revealed, which, combined with the structural and electronic structure insight, may hold the key to a better
8.8 Sulfiding Co on Au(111)

An interesting spin-off study from the experiments with the promoted CoMoS is concerned with the formation of cobalt sulfides on the Au(111) surface shown in Fig. 8.1(a) and (b). The large transport of Co to the Au(111) step edges and the formation of large cobalt sulfide structures during synthesis conditions immediately suggest a large mobility of Co in the presence of sulfur.

To test this, experiments were conducted by depositing an initial amount of Co onto the clean Au(111) surface and exposing the clusters situated in the herringbone elbows to H\textsubscript{2}S at room temperature while imaging with STM. The sequence of STM images shown in Fig. 8.8 are in situ snapshots taken of the Co islands on the Au(111) terraces as a function of the H\textsubscript{2}S exposure. Here the surface coverage is shown to decrease exponentially with the total exposure. This occurs with a simultaneous build-up of large islands at the Au(111) step edges with a similar structure as those in Fig. 8.1(a) and (b), and the experiments thus confirm the assignment of these to a cobalt sulfide. Remarkably, the migration of Co in a sulfiding environment is found to be very pronounced at room temperature.

It was not possible to isolate individual migrating species in STM images in order to solve their nature, but since the Co clusters in time-resolved STM sequences reduce their size gradually, it is speculated that the migrating species are relatively small, consisting of only a couple of Co atoms. This suggests that the S-enhanced ripening occurs by a gas-induced weakening of the metal-metal bonds in the cluster and the formation of highly mobile Co-S complexes. A similar picture was recently suggested to explain the S-enhanced ripening of Cu islands on Cu(111) films, where the formation and diffusion of ad-Cu\textsubscript{3}-S\textsubscript{3}.

Figure 8.8: Sequence of STM images 678×740 Å\textsuperscript{2} showing Co clusters on Au(111) exposed to 4×10\textsuperscript{-8} mbar at room temperature. The images show the distribution of surface structures after exposures of (a) 4 L, (b) 122 L and (c) 177 L, respectively.
was found be particularly favorable in a theory study [211]. The large mobility of Co-S species may explain why the co-deposition of both Co and Mo is particularly efficient for the purpose of synthesizing CoMoS. A synthesis of MoS$_2$ followed by subsequent deposition of metallic Co does not facilitate the formation of CoMoS but merely results in the creation of well-separated MoS$_2$ islands and sulfided Co at the step edges. Hence, initial intermixing of the two metals appears crucial for the formation of CoMoS.

Generally, gas-induced cluster dynamics and sintering are key issues in heterogeneous catalysis [13, 14, 20, 212], since the processes may lead to loss of active surface area and a serious reduction in catalyst activity and selectivity. With a better fundamental understanding of the gas-adsorbate interaction governing the processes, countermeasures could be taken to prevent the damage to a number of operating catalyst systems. This includes the Co promoted HDS catalyst where the primary concerns is to prevent phase separation of the Co and Mo during initial activation.

If highly stable and diffusive Co$_x$S$_y$-complexes generally form independently of the substrate, the present STM results hold interesting perspectives in relation to the optimum industrial synthesis of Co-promoted catalysts. This was studied in work by the group of Niemantsverdriet, who synthesized CoMoS model systems by spincoating Co and Mo oxide compounds on different substrates followed by sulfidation in H$_2$S [80, 81]. Here, it was shown with XPS spectroscopy that a key factor, controlling the activity of CoMoS catalysts, was the ability of the support to prevent phase separation, i.e. to keep the Co from being sulfided at lower temperatures than Mo. For industrial purposes this tendency can be retarded by adding so-called chelating agents, which are large organic molecules with the ability of confining the Co until it is appropriately imbedded in the CoMoS [81, 213, 214]. Further insight into the detailed processes controlling the diffusion of Co-S species may lead to a better understanding of chelating agents and the development of better synthesis processes.
Chapter 9

Summary and Outlook

Most knowledge on the atomic-scale structure of the MoS$_2$-like active phase of HDS catalysts has previously been inferred from bulk properties down-scaled to the appropriate size of nanoclusters. This deficiency and a lack of direct insight has for a long time hampered a detailed understanding of the mechanisms underlying the catalytic activity, simply because it is intimately connected only with defect sites at the edges of such nanoclusters. A prerequisite for a deeper understanding is atomic-scale elucidations of the composition, geometric structure and electronic structure of the catalyst particles. The experimental results in this thesis represent the first direct real space information on the shape and edge structure of MoS$_2$ nanoparticles and establishes a new picture of the active sites pertaining to the cluster edges.

The new pieces of information presented in this thesis are obtained by use of the surface science approach to catalysis. The large knowledge generated in the surface science community during the last many decades is exploited to synthesize a realistic catalyst model system for the hydrotreating catalyst consisting of an ensemble of approximately 30 Å wide single-layer MoS$_2$ nanoclusters supported on a Au(111) substrate. The model system is directly accessible to studies with STM which provides information on the morphology and the detailed edge structures of the nanoparticles.

The STM studies reveal that the morphology and edge structures of the catalytically important MoS$_2$ edges deviate geometrically and electronically from simple expectations based on bulk properties. Under sulfiding conditions, the MoS$_2$ nanoclusters adopt a triangular morphology, implying that one of the two low-indexed edge terminations, the Mo edge or the S edge, is far more stable than the other. The particular type of edge terminating the triangular clusters is found exhibit an extraordinary high electric conductance compared to the rest of the cluster due to one-dimensional metallic edge states. The existence of such subtle electronic effects at the potentially catalytically important edges has not previously been emphasized. In an interplay with theoretical studies, the presence of such states is found to profoundly influence the STM imaging, and by STM simulations the edges are identified as fully sulfur-saturated Mo edges.

When adsorbing hydrogen and thiophene as probe molecules, a remarkable chemistry associated with the MoS$_2$ edge is unravelled. Upon exposure of the MoS$_2$ nanoclusters to
Summary and Outlook

atomic hydrogen, the first direct evidence is presented of the existence of edge S vacancies, believed to be active sites in the HDS reaction. Furthermore, the activation with hydrogen leads to a strong interaction with thiophene. New sites located on the metallic edge states are found to be able to hydrogenate and facilitate C-S cleavage in thiophene – the first step of HDS. The reactivity of the MoS$_2$ clusters may then be explained by a two-step process in which molecules are first adsorbed on the new sites and hydrogenated by S-H groups on the edge followed by S extrusion at the S vacancies. This is an entirely new way of thinking about the reactivity of the active clusters.

A large portion of the present work has been concerned with the fully sulfided triangular single-layer MoS$_2$ nanoclusters, since these were the starting point in the model system. Under reducing conditions both the morphology and edge structure of the MoS$_2$ nanoclusters is found to be influenced in a profound way. The model system consisting of hexagonal MoS$_2$ nanoclusters thus marks another starting point for future investigations on e.g. the adsorption of hydrogen and thiophene since the clusters expose different edge, i.e. the S edge and a Mo edge with a lower S coverage. Noticeably, the Mo edge still exhibits the bright brim associated with an electronic edge state may thus also hold adsorption sites for e.g. thiophene, whereas the S edge maintains a coverage of H atoms believed to enter in a hydrogenation reaction.

It should be stressed that it still remains to be investigated if the model system is active under operation conditions, and for this purpose it would be interesting to perform the reactivity test in batch flow reactors. Since the morphology is well-characterized, the reactivity of the active sites may be determined exactly by the turn-over-frequency (product molecules per active sites per time). Performed in a reactor cell at high pressures and high temperatures, such experiments may also reveal the state of catalysts under these conditions. In the present studies, new information on the significance of the pressure gap was obtained by synthesizing the MoS$_2$ nanoclusters at the working reaction temperature and in a low-pressure gas-mixture mimicking the reducing conditions during HDS. In order to fully bridge the pressure gap, investigations at realistic pressures should be performed and for this purpose in situ measurements by means of a dedicated high-pressure STM would be ideal. In our laboratory, atomic-resolution at pressures up to 1 bar was recently demonstrated [9,10], and an implementation of this highly stable STM design in a reactor cell, like the setup of Hendriksen et al. [26], may prove to be a very powerful tool to investigate the above-mentioned issues on both the morphology and reactivity.

The main finding of the experiments on the Co-promoted phase, is the elucidation of the exact position of the Co promoters in CoMoS nanoclusters. The presence of the Co atoms has a dramatic influence on the morphology of clusters, a fact which is linked to a preference for Co to be located at only the S edges. The inclusion of Co is found to affect the electronic and geometric structure of the edges, and preliminary experiments with hydrogen and thiophene reveal that the Co facilitates an increased interaction with S-containing molecules, i.e. evidence of a promotional effect. A general method to synthesize CoMoS particles is described, and further information on the promoting role of Co may be revealed by extending the present studies to also include the effect of reducing conditions or the adsorption of more complex S containing molecules.

The results presented in the thesis are evidently by no means exhaustive and there is ample room for refinements and new initiatives in future studies. Compared to earlier efforts
studying the structure of the catalysts, the materials gap is narrowed considerably in the present model system since it captures the essentials of the cluster nature of the active material. To further bridge the materials gap, other model substrates should be considered for the growth of MoS$_2$ nanoclusters. Oxidic supports like $\gamma$-Al$_2$O$_3$ or carbon are employed as carriers in real HDS catalysts and the model system may be extended by employing models of these surfaces in the form of either Al$_2$O$_3$ or highly oriented pyrolytic graphite (HOPC). Well-ordered and electrically conducting Al$_2$O$_3$ thin films may be formed by oxidizing a Ni$_3$Al(111) [215] or NiAl(110) [19], a method which has been used extensively to study supported Pd nanoclusters in our laboratories. Alternatively, one may employ single-crystal $\alpha$-Al$_2$O$_3$, which is non-conducting, and study it with Atomic Force Microscopy [17, 216]. If the MoS$_2$ nanoclusters can be formed on these flat substrates, new studies may provide information on the effect of the support.

The main experimental technique employed in the present studies is the STM. This is a natural consequence of the fact that the study was aimed at obtaining detailed atomic-scale insight into the structure of MoS$_2$ nanoclusters. The characteristics of the catalyst model system was optimized for this purpose, and although it would be highly desirable to have the new results on the reactivity verified by e.g. spectroscopy measurements, the rather low amount of active sites present only at the edges of the highly dispersed MoS$_2$ nanoclusters renders an equally detailed, spectroscopy-based characterization a very challenging and maybe impossible task. At present, the most conceivable way to proceed is to continue bridging the materials and pressure gaps with similar model studies and then compare the characteristics directly with the large database of in situ studies performed on real supported HDS catalysts.

The present study also applies in a more general scope. The interest in studying nanosized materials is bigger than ever, and the approach presented should be applicable to inorganic clusters deposited on conducting substrates in general. Up to now, much focus has been on metal and semiconductor nanocstructures, whereas the knowledge about transition-metal sulfide nanoclusters is rather limited. Such clusters are, besides as catalysts, also important as lubricants [217], and as models of the active part of some enzymes [106, 218].
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