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## **Microscopy and spectroscopy on model catalysts in gas environments**

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# Chapter 1

## Introduction

## 1.1 Catalysis

Some of the most urgent challenges of our time, as defined by the United Nations [1], are the supply of clean and affordable energy, the reduction of pollution and waste on land, in air, and in water, counteracting climate change, and producing enough food for the growing world population. In all of these areas catalysis can and is playing a role: Refining fossil fuels and increasing the cleanliness of the products, which are used for transportation as well as the chemical industry, relies heavily on catalysts [2]. This has not changed with the search for more sustainable energy sources [3]. The use of solar and wind energy relies on more efficient energy-storage methods like chemical storage, which gives the need for catalytic conversion of chemicals. A hydrogen economy would not only need catalysts for the hydrogen production [4], but they are also an integral part of retrieving the energy in fuel cells. Additionally, catalysis for CO<sub>2</sub> conversion is being researched extensively [5]. In the effort to reduce pollution, catalysts can convert harmful substances into less harmful ones after or before they are released into the environment [6], with the most well-known example being the 3-way catalyst in combustion engine vehicles [7]. The use of catalysts for the production of fine chemicals, including pharmaceuticals [8], reduces the amount of energy needed and can prevent unwanted side products. Last, food production has increased significantly due to the catalytic production of fertilizer [9] and depends on enzymes for food processing [10]. Given this vast range of applications, it is not surprising that catalysts come in various forms. One distinguishes the fields of homogeneous catalysis, heterogeneous catalysis including electrochemistry, and biocatalysis [11,12]. Catalysts can be organic like the enzymes in your body, molecules and complexes, or surfaces; they can contain metals or oxides, and can even be made from waste [13] or consist of single atoms [14]. The activity of some catalysts is induced by photons [15] or plasma [16]. The general definition of catalysis is the same in all these fields: Without being a reactant or product itself, the catalyst reduces the barrier for the reaction and thus increases the reaction rate, makes the reaction less energy-consuming, and/or more selective to a specific reactant or product [12].

## 1.2 Surface Science: Atomic-Level Understanding

This thesis focuses on heterogeneous catalysts, in particular solid surfaces catalyzing gas-phase reactions. In this case the reactant(s) usually adsorb on the surface, possibly dissociate, and react, followed by the desorption of the product(s). In contrast to this Langmuir-Hinshelwood mechanism, one of the reactants can also react directly from the gas phase without prior adsorption in an Eley-Rideal mechanism [17] or atoms

from the catalyst can be removed and replaced again during the reaction via a Mars-van Krevelen mechanism [18]. In any of the three cases the so-called catalytic cycle is closed when the reaction has taken place and the catalyst has returned to its initial state [11].

Generally, it is clear that research of catalysts can improve their performance and therefore make their application more cost-effective and energy-efficient. Surface science in particular aims at fundamentally understanding the origin of the catalytic activity by studying the interaction of molecules with surfaces on the atomic level. This includes adsorption, diffusion, and dissociation behavior, as well as the reaction with other (adsorbed) molecules. Atomic-level studies are facilitated on simplified model systems under well-controlled conditions as well as in computational chemistry [19]. Certain techniques such as temperature-programmed desorption [20], molecular beam studies [17], and electron diffraction (see Section 2.5) inherently require ultra-high vacuum environments, whereas other techniques like X-ray photoelectron spectroscopy (see Section 2.4) simply take significantly less technical effort when performed in vacuum and on conductive samples. Atomic-scale imaging with scanning tunneling microscopy (see Section 2.3) is easiest applied on atomically flat and conductive surfaces such as metal single crystals. The results that such conventional surface science achieves are vast and a necessary piece of the puzzle that is understanding the catalytic process in its whole. Therefore, I wish to emphasize the importance of such research, before moving on to motivating an additional direction within surface science in the following sections.

### 1.3 Complex Model Catalysts: Bridging the Materials Gap

The difference between flat, single-crystalline surfaces studied in conventional surface science and industrially used powder catalysts, often consisting of metal particles and oxide supports, including many different possible structures, is what we call the materials gap [21]. Ideally the most stable face of a single crystal consists of large, flat terraces. However, often low-coordinated surface sites like steps, kinks, and defects can be significantly more active for interactions with gas-phase molecules than the terrace sites [22]. Chapter 5 of this thesis exemplifies the use of the most closed-packed face of a metal single crystal, Co(0001), which is, however, expected to have a significant number of steps and defects due to limitations in the preparation method. The effects of low-coordinated sites can be studied more systematically on stepped single-crystal faces, especially by comparing their behavior to the closed-packed ones [22], which is also possible by computational methods [23]. Recent progress has also been made in continuously varying the step density over a large range by studying curved single

crystals [24].

Oxide materials relevant for catalysis can be investigated in the form of thin oxide films deposited onto metal single crystals [25]. These are additionally relevant for certain other applications [26]. Due to the conductivity of the metal substrate underneath, thin films can still be studied with the same techniques as metal single crystals. However, the structure of deposited films depends on the lattice mismatch and the interaction with the substrate, such that it can differ significantly from the bulk structure [27–29]. Additionally, an influence of the substrate on the electronic structure of the oxide and thus its interaction with gases cannot be excluded [25,29]. This can be avoided by directly using bulk oxide single crystals [30]. We do this in Chapter 3 of this thesis with ZnO(10 $\bar{1}$ 0), where we also mention certain challenges associated with its use.

The world of single-crystal-based model catalysts can be vastly expanded by the deposition of various metal [31], oxide [29], and/or sulfide [32] nanoparticles onto the single-crystal surface. By thus combining the different components that are contained in industrial catalysts, the interface region between them can be studied. Often the oxide ‘support’ is not merely a template keeping the active metal nanoparticles in place but rather an active component of the catalyst influencing its activity, selectivity, and/or poisoning behavior [31]. So-called strong metal-support interactions can lead to substantially different geometrical and electronic structures in the interface region [33]. In Chapter 4 of this thesis we investigate a complex model catalyst consisting of a metal single crystal with oxide nanoparticles on top, TiO<sub>2</sub>/Au(111). Such a so-called inverse model catalyst can more easily be studied with methods requiring conductivity. Directly comparing an inverse model catalyst to its non-inverse counterpart, nanoparticles of the metal on a single crystal of the oxide, can shed light on the influence of nanoparticle morphology, different crystal faces, and electronic structure on the activity [34,35].

## 1.4 In Situ Studies: Bridging the Pressure Gap

Another disparity between conventional surface science and realistic applications is the so-called pressure gap [21], which refers to the pressure difference between vacuum studies (in 10<sup>−11</sup> mbar to 10<sup>−3</sup> mbar) and industrial catalysis at at least atmospheric pressures up to even hundreds of bar [36]. As the interaction of molecules with catalyst surfaces but also the structure of the surfaces itself can strongly depend on the absolute pressure, efforts have been made to expand surface-science techniques to also be applicable at near-ambient to ambient gas pressures, the so-called in situ approach [37]. When, additionally, the products of the catalytic reaction are detected in the gas phase, one can speak of an operando technique [21].

Ambient-pressure imaging of surfaces has been achieved using optical microscopy [38], transmission electron microscopy [39], X-ray microscopy [40], scanning tunneling microscopy [41–44], and atomic force microscopy [45], which is more suited for the study of oxide samples. The so-called ReactorSTM [44], which is used in Chapters 3 and 4 of this thesis, incorporates a small-volume flow-reactor cell into a vacuum chamber. In this way the gas flow and pressure can be regulated precisely and a swift change between vacuum and ambient conditions of up to 6 bar gas pressure and 600 K surface temperature is possible. As such the reactor microscope can show the structure of the active surface and shed light on reaction mechanisms for a variety of catalysts and reactions [46–48].

X-ray absorption techniques can give spectroscopic information and unravel local electronic structure in situ [49], whereas in situ surface X-ray diffraction can determine the structure of the surface during the reaction [50]. The latter can be combined with laser-induced fluorescence probing the gas distribution above the catalytically active surface [51]. Reaction intermediates and products can be identified with infrared and UV-VIS absorption techniques, like vibrational and Raman spectroscopy, which are applied in situ as well [52,53].

A particularly challenging but also particularly useful technique to apply at elevated pressures is X-ray photoelectron spectroscopy. Particularly useful because adsorption behavior of molecules as well as chemical states of the catalyst material can strongly depend on the gas pressure. Particularly challenging because the technique relies on the detection of electrons, which can only travel short distances in situ. Nonetheless, near-ambient pressure X-ray photoelectron spectroscopy has been made available to a large number of catalysis researchers [54], especially through user facilities. Chapter 5 of this thesis presents an example of a near-ambient pressure X-ray photoelectron spectroscopy study conducted using synchrotron X-rays.

Apart from those techniques which are widely used now, new techniques are being adapted to in situ use as shown in proof-of-principle studies. For example synchrotron X-ray assisted scanning tunneling microscopy combines local structural with local spectroscopic information [55]. Simultaneous non-contact atomic force microscopy and scanning tunneling microscopy images corrugation at the same time as electronic structure [56]. Additionally, there is considerable effort made in expanding the use of X-ray photoelectron spectroscopy from near-ambient to fully ambient pressures [57,58]. The list of in situ techniques mentioned here is most likely not complete.

As we will see in all three systems investigated in this thesis, in situ studies on complex model catalysts do not only allow for the observation of new structures and behaviors, but also bring along with them a new set of challenges caused by low concentrations of impurities in materials and gases. Before diving into the experimental results in Chap-

ters 3 to 5, the interested reader can find a detailed explanation of the surface-science techniques used, in vacuum as well as in situ, in the following chapter.