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## **Imaging complex model catalysts in action: From surface science towards industrial practice using high-pressure scanning tunneling microscopy**

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# Chapter 1

## Introduction

Whether it cures a disease, causes a colorful explosion in fireworks, or forms glittering crystals, chemistry has the power to amaze. Much of this amazement is caused by the seemingly incomprehensible relation between cause and effect when materials react. In 1727, the early days of chemical research, a frustrated Hermann Boerhaave noted [1]:

*“For chemistry is no science form'd à priori; 'tis no production of the human mind, framed by reasoning and deduction: it took its rise from a number of experiments casually made, without any expectation of what follow'd; and was only reduced into an art or system, by collecting and comparing the effects of such unpremeditated experiments, and observing the uniform tendency thereof. So far, then, as a number of experimenters agree to establish any undoubted truth; so far they may be consider'd as constituting the theory of chemistry.”*

Fortunately, the modern-day chemist can rely on extensive fundamental understanding to explain the how and why of chemical reactions. However, *predicting* chemistry is much more difficult than *explaining* it after the fact. In practice therefore, chemical research remains highly empirical. This is particularly true in the search for catalysts, compounds that accelerate a chemical reaction without being consumed (except for some slow degradation). To find new catalysts, chemical companies mostly use a brute-force approach, i.e. trial and error guided by the empirical trends from previous trial-and-error studies. While this approach has proven fruitful for optimizing the chemical processes that we employ today, the lack of fundamental understanding of catalyst behavior hampers the introduction of new chemistry.

Now that society is more and more aware of the effects that humanity has on the environment, there is a growing desire for a transition from fossil-oil-based chemistry to sustainable chemistry. Such a transition requires a complete makeover of the chemical industry, with many new industrial catalytic processes to be developed. The current empirical approach for finding catalysts may therefore no longer suffice. Hence, a vital next step in catalytic research is to increase our understanding from the point where we can give an explanation of catalysis to the point where we can formulate predictive guidelines.

## 1.1 Understanding a catalytic process

Any chemical reaction consists of one or more elementary bond breaking and/or bond making steps, which rearrange the way the atoms in the reactant molecules are bound to one another. Such a reaction can either consume or release energy. To calculate this change in reaction energy, we use the chemical potential of each molecule in the reaction, which describes its relative stability under the applied conditions of temperature and concentration at which molecules of the same species are present in the medium. Throughout this thesis, the chemical potential will be defined as:

$$\mu = E + E_{ZP} - ST + k_B T \ln(P) + C_P T \quad (1.1)$$

In equation 1.1,  $E$  is the electronic energy of the molecule at 0 K,  $E_{ZP}$  is the molecule's vibration energy at 0 K,  $k_B$  is Boltzmann's constant,  $T$  is the temperature,  $S$  is the entropy of the molecule,  $P$  is its (partial) pressure (for gases), and  $C_P$  is its heat capacity. With this definition, the chemical potential of a molecule is the energy gained from putting it together using electrons and ionic cores, and bringing it to a certain temperature and pressure. The change in Gibbs free energy accompanying the reaction  $w A + x B \rightleftharpoons y C + z D$  is:

$$\Delta G_r = y\mu_C + z\mu_D - w\mu_A - x\mu_B \quad (1.2)$$

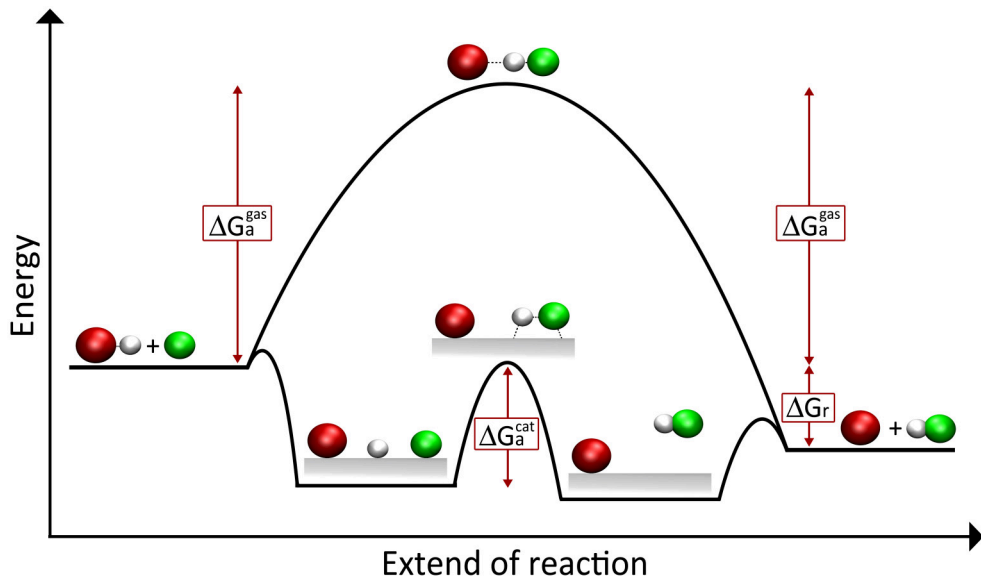
If this number is negative, the net forward reaction is thermodynamically favorable, meaning that at some point it will occur. It does, however, not tell us anything about the reaction kinetics. For example, the reaction of oxygen with the sugar, fat and protein of the human body to form  $\text{CO}_2$  and  $\text{H}_2\text{O}$  is thermodynamically favorable, but fortunately extremely slow.

To go from one atomic arrangement to the other, the reactant molecules usually have to be distorted into an unfavorable configuration before new bonds can be formed. Such a distortion costs energy, thus creating a barrier for the reaction to occur (see Figure 1.1). In the simplest approximation and for a reaction consisting of one elementary step, the net reaction rate can be determined from the energy barrier and reaction energy by:

$$r = [A][B] \frac{k_B T}{h} e^{-\Delta G_a/k_B T} - [C][D] \frac{k_B T}{h} e^{-(\Delta G_a + \Delta G_r)/k_B T} \quad (1.3)$$

In equation 1.3,  $[A]$ ,  $[B]$ ,  $[C]$ , and  $[D]$  are the concentrations or partial pressures of molecules A, B, C, and D,  $h$  is Planck's constant and  $\Delta G_a$  is the activation barrier of the reaction. For many uncatalyzed reactions,  $\Delta G_a$  is very large compared to  $k_B T$ , leading to very low reaction rates. A catalyst lowers the reaction barrier by providing a different reaction pathway (see Figure 1.1). Such a catalytic pathway typically consists of the molecules binding to the catalyst, dissociating, forming new bonds, and

desorbing from the catalyst (see Figure 1.1). For a good catalyst, the binding strength of the reactant and product molecules to the surface is balanced (Sabatier's principle)[2]. Strong binding makes it easy for the reactants to dissociate, but inhibits the desorption step. Weak binding, on the other hand, insufficiently aids the dissociation of the reactants.

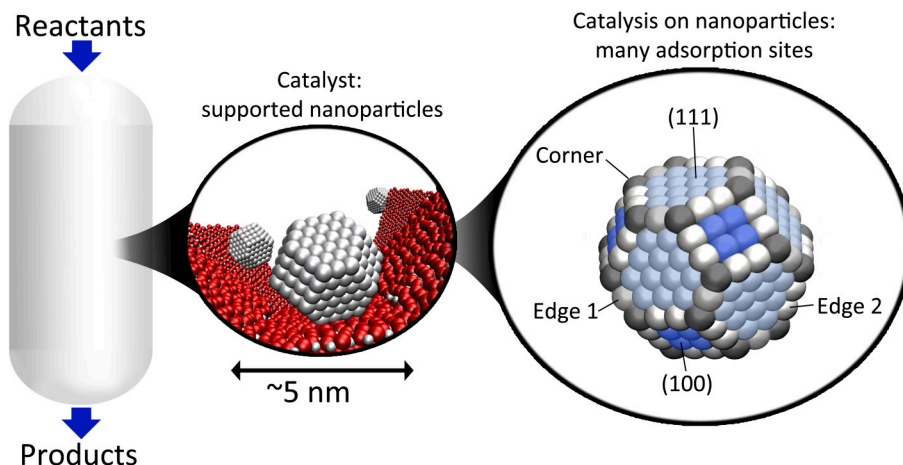


**Figure 1.1:** Illustration of the elementary steps in a chemical reaction. In the gas phase, a large free energy barrier needs to be overcome for the reaction to proceed. A catalyst offers an alternative pathway with lower energy barriers, thus speeding up the reaction.

In many cases, reactant molecules can bind to one another in several ways, yielding a variety of products. For example, a mixture of CO and H<sub>2</sub> can produce methane [3], methanol [4], ethanol [5], and alkanes [6]. To control which product is formed, catalysts are tuned to selectively accelerate the reaction forming only one product.

Most industrial catalytic processes are examples of heterogeneous catalysis: gaseous and/or liquid reactants interact with a solid catalyst. At the atomic level, the surface of the catalyst is very inhomogeneous. Most catalysts consist of nanoparticles fixed on a chemically robust oxide support such as Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, or TiO<sub>2</sub> (see Figure 1.2). The nanoparticles provide a variety of surface sites to bind the reactant molecules, each with its own binding properties and hence catalytic activities. Even a simple, pure fcc metallic nanoparticle, with only (111) and (100) type facets, has 5 different atomic nearest-neighbor configurations, providing 12 different adsorption sites. The nanostructuring of the support and the use of additives and promoters increase this number drastically. Another addition to the complexity of catalysis is the fact that the reaction rate on all the different binding sites depends on the temperature and the concentration of reactants and products at the catalyst surface (see equation 1.3).

Hence, the mass and heat transport within the reactor also play a key role in the overall behavior of the process. These considerations show that it is far from trivial to couple cause and effect in catalytic research.



**Figure 1.2:** Essence of the structure of an industrial catalyst. The reactor is filled with a porous oxide material that supports the catalytic nanoparticles. The nanoparticles offer a variety of adsorption sites to which the reactants can bind. The structural complexity of the catalyst, together with its dynamic nature and the interplay with the mass and heat transfer in the reactor, make the relation between cause and effect extremely complex in catalysis.

## 1.2 The role of surface science

To disentangle the many factors that determine how well a catalyst works, one needs to be able to vary them independently, so that cause and effect are clear. For industrial catalysts, full control over the structural and chemical properties is not feasible, however. The surface science approach resolves this issue by using simplified model catalysts, in which some of the structural complexity is eliminated. The aim of surface-science experiments is to have a very high degree of control over all parameters in the experiment and to have complete understanding of the surface chemistry at the atomic level.

To allow for such control and understanding, surface science experiments are traditionally performed on polished single crystals that expose predominantly one or two atomic arrangements over their entire surface [7]. Furthermore, the gas environment is controlled by working in ultrahigh vacuum ( $<10^{-6}$  mbar), so that only gases that are leaked into the system reach the sample surface. The additional advantage of the vacuum is that the surface can be studied using refined techniques

that rely on the interaction of electrons, ions, or atoms with the sample. The simple structure of the single-crystalline model catalyst allows for comparison to density functional theory (DFT) calculations, which describe the (electronic) structure and energetics of a limited number of atoms in great detail [8].

The bottom-up approach described above has allowed for a very good understanding of fundamental adsorption/desorption phenomena. If one is interested in the details of a specific catalytic process, however, single crystals in vacuum are too simplified to be representative of industrial catalysis. Two main oversimplifications can be identified: the *materials gap* and the *pressure gap* [9]. The materials gap originates from the fact that the same type of adsorption site on a catalyst nanoparticle and a single crystal may have very different properties. The electronic structure of a supported nanoparticle deviates from that of bulk material because of its small size and the interaction with the catalyst support [10,11]. Furthermore, some types of adsorption sites that exist on a nanoparticle cannot be created on a single crystal. The pressure gap further complicates matters due to the fact that the shape and surface structure of nanoparticles can change at elevated pressures [12,13]. Such surface reconstructions require the combination of a high driving force for adsorption and sufficient atomic mobility, i.e. high temperature. This combination can often not be achieved in vacuum.

To reconcile the fundamental experiments with industry, the modern trend in surface science is to bridge the materials and pressure gaps step by step. For the materials gap, this is typically achieved by the deposition of nanoparticles on single-crystalline supports. Theoretical models follow this development, although the computational cost limits the particle size that can be handled [11–15]. The effects of elevated pressures and temperatures can be modeled by straightforward addition of entropy terms (see equation 1.1), or in more detail using microkinetic modeling [16,17]. From the experimental side, the main challenge to bridge the pressure gap is the development of instrumentation that allows characterization of the catalyst's structure while it is operating [9,18,19]. One could imagine performing measurements in vacuum before and after using the catalyst. However, many of the reconstructions occurring on catalysts are reversible and will therefore not be visible in such measurements [9]. Hence, to gain proper understanding of how a catalyst works, *operando* structural and chemical characterization of well-defined nanoparticle model catalysts is essential.

### 1.3 In this thesis

In my PhD work, I have studied aspects of both the materials and the pressure gap using scanning tunneling microscopy (STM). This technique relies on measuring the tunneling current between the (conductive) sample surface and a sharp metal wire (the STM tip). The current decays from short circuit when tip and sample make

physical contact, to practically zero at a tip-sample distance of roughly 1 nm. Hence, the tunneling current can be used to track the morphology of the sample surface with atomic precision. A detailed treatment of STM can be found in Ref. [20].

Although STM is primarily used to study flat substrates, it can also be employed to characterize supported nanoparticles. In Chapter 2, I have used the combination of STM and X-ray photoelectron spectroscopy to investigate the nucleation and growth of MoO<sub>x</sub> on Al<sub>2</sub>O<sub>3</sub>/NiAl(110). The aim of this study is to find handles for controlled preparation of complex model catalysts. Most work on such models has been performed on pure metallic nanoparticles [21–24]. From these studies, a clear picture has emerged of how the metal-support interaction influences the nucleation process. In Chapter 2, I extend this type of analysis to metal oxide particles.

Using a special scanning tunneling microscope, the ReactorSTM [25], I have performed measurements under high-temperature, high-pressure conditions. In Chapter 3, I discuss the structure of MoS<sub>2</sub> nanoparticles on Au(111) during the industrially important hydrodesulfurization reaction, in which sulfur is removed from organic molecules:



Zooming in on the atomic level detail of catalysts during this reaction, I investigate how the structure of the MoS<sub>2</sub> particles depends on the partial pressures of the reactants/products. A comparison to DFT calculations shows to what extent the reaction kinetics affect the MoS<sub>2</sub> structure.

In Chapter 4, I study the formation of Au surface oxides on WO<sub>3</sub>/Au(111) and ReO<sub>3</sub>/Au(111) inverse model catalysts. Such oxides could be important reaction intermediates on Au-based oxidation catalysts, but their existence under reaction conditions is questioned. Using the temperature dependence of the Au oxide coverage, I show that Au oxides are thermodynamically favored over a wide range of conditions.

In the last Chapter of this thesis, I discuss how one can increase the information depth from high-pressure STM by combining it with X-ray absorption spectroscopy (XAS). In a proof-of-principle study, I show that our integrated STM-XAS set-up is able to measure the X-ray-induced changes in the tunneling current, which opens the way to obtaining local chemical information with nanometer spatial resolution.



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