Oxidation catalysis on Pt and Au : complexity of simple chemistry

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Chapter 1

Introduction

Several opportunities arise to a chemist to make oneself useful. One can unravel the origin of life and try to understand the workings of a living cell [1], without a doubt the most sophisticated chemical system known to man. One can even go beyond life on this planet, by studying the role of chemistry in the history of the universe [2]. Chemists with a more practical mindset can design and synthesize new materials, such as solar cells or batteries [3], or synthesize the most complex molecules [4], such as maitotoxin, with the chemical formula $C_{164}H_{256}O_{68}S_2Na_2$ [5]. Instead of making small amounts of novel and daunting molecules, I am interested in the understanding of how to make rather simple molecules in the largest quantities and with the highest efficiency. These are the goals of the field, called heterogeneous catalysis.

Catalysis and the catalyst, the active agent of this process, are widely familiar terms for the general public because the catalytic converter is a vital component of the modern-day car. In an automotive exhaust, it plays an important role: Toxic pollutants are transformed into less harmful gases in a fraction of a second.

A second immensely important example of catalysis is the production of fertilizers. To make fertilizers, hydrogen produced from, e.g., natural gas, and molecular nitrogen are catalytically converted in several steps via ammonia to nitric acid. One of these steps, the synthesis of ammonia, has been awarded with two Nobel prizes [6, 7] and has been labeled as the most influential achievement of the twentieth century [8]. This process is highly energy demanding thus making improvements in catalyst efficiency both economically and environmentally attractive. A final illustration of catalysis is the formation of liquid fuels from syngas[1] [9]. These fuels can be carbon neutral if syngas is made from biomass. These examples show that catalysis plays a key role in two of the eight millennium goals [10].

1.1 Foundation of catalysis

Any spontaneously occurring chemical reaction proceeds by virtue of a decrease in the so-called free energy. This is analogous to a stream of water that will only flow if the destination is lower than the starting point. The spontaneity of a chemical reaction does not give us any information about the activity. For example, it is well known that diamond transforms to graphite under everyday conditions. The rate of this reaction is, luckily, completely negligible.

Reactants in a chemical process often need to cross an energetic barrier, which finds its origin in unfavorable configurations the molecules have to adopt while transforming from reactant to product. The most unfavorable configuration has the highest energy and is called the transition state. These transition states are either stabilized by the interaction with a catalyst, or the catalyst has the ability to provide an alternative pathway with a lower energy transition state. In both cases, the catalyst decreases the reaction barrier and increases the reactivity. This principle is depicted in Figure 1.1.

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[1] a mixture of CO and H_2

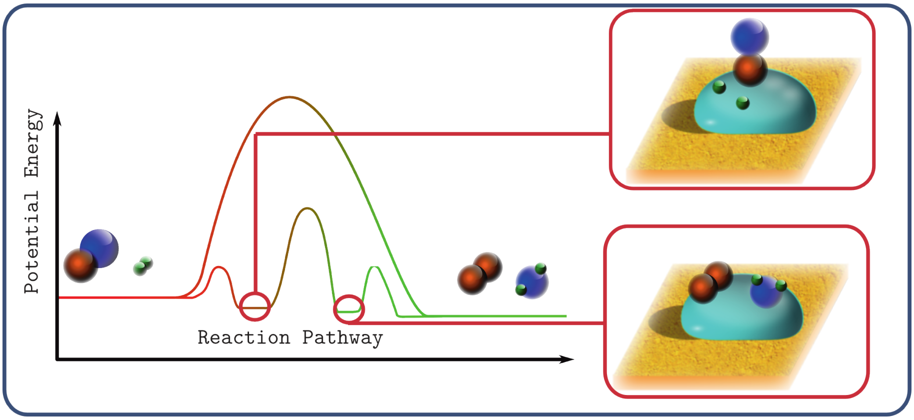

Figure 1.1: Schematic view of the principle of catalysis. Two reactants, e.g., NO and H_2, need to overcome a large barrier to react without a catalyst. The catalyst can stabilize the highest point on this barrier, by reducing the energy height of this transition state. In this way, the total barrier is lowered. Alternatively, the catalyst can provide a different reaction pathway with more stable transition states. In both cases, the catalyst increases the rate of the reaction, but it does not alter the relative difference between the initial and final energies. The insets show examples of intermediate stages in a heterogeneous catalytic process: The first shows the reactants adsorbed on a supported nanoparticle, while the second shows the adsorbed products. (Note that the numbers of red atoms, e.g., nitrogen, are not the same on the left and right sides of the barrier. For the full reaction, two N atoms are required, originating from two NO molecules and in total 4 green atoms, e.g, H atoms.)

1.2 Challenges in catalytic research

Industrial catalysts are highly complex systems. A typical class of catalysts consists of metallic particles ranging from a few to several tens of nanometers in diameter. These particles are often supported on porous oxides, from which three-dimensional pellets are formed. These structures at different length scales are shown in Figure 1.2 for typical heterogeneous catalysts.

The first step in understanding catalysis is to gain insight into the structure and reactivity of the different parts of the catalyst and their interfaces. The chemical reactivity can be obscured by physical processes, such as gas phase diffusion and heat transfer. The total reactivity depends on both chemical and physical properties of the catalytic materials. These properties are not static, however, and can change as a function of temperature, gas composition, and time.

The difficulty in understanding catalysis is not so much the catalyst's inherent complexity, but rather the poor experimental capabilities to fully characterize its properties. This characterization needs to be performed either under so-called *operando* conditions or under *in situ* conditions, i.e., on a working catalyst under reaction conditions or in an environment that mimics the reaction conditions. The definitions of operando and in situ are not very strict and the terms have been used interchangeably. However, the main difference between operando and in situ conditions is that the former requires a working catalyst. The active catalyst changes the local gas environment into a

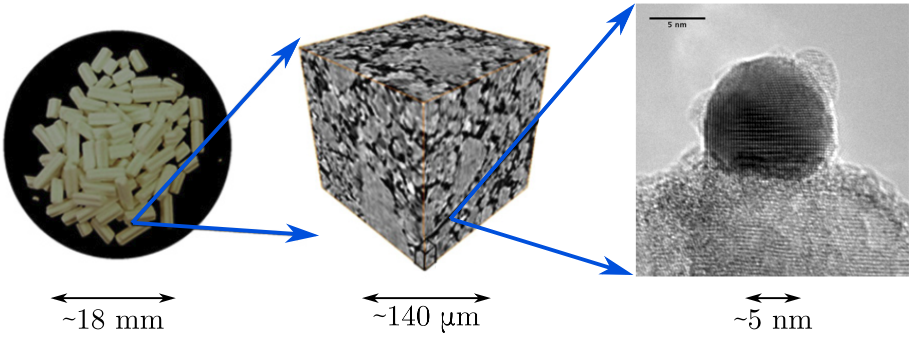

Figure 1.2: Illustration of the complexity of a catalyst on different length scales. The left image shows macroscopic pellets, which are typically used to fill an industrial reactor; optical photograph. The middle image shows the porous structure of the supporting oxide; X-ray microtomograph. The right image shows an individual nanoparticle on the oxide support (different catalyst); transmission electron micrograph. Left and middle images were adapted from Reference 11, while the right image was adapted from Reference 12, with permission from Elsevier and MDPI, respectively.

mixture of reactants and products, which leads to a more realistic measurement, which is better comparable to the industrial process. The activity of the catalyst should be measurable and measured in order to qualify as an operando measurement.

Both operando and in situ mean that experiments need to be performed under (semi)realistic conditions, i.e., at high pressure and elevated temperature. However, most techniques are not capable of measuring under these conditions. The tools that can be applied under these harsh conditions usually require specialized experimental setups and often only give a fraction of the information needed to fully characterize the catalyst chemically and physically.

An alternative strategy that has allowed characterization of the catalysts to a higher degree is the so-called *post mortem* research. In this method, a fresh catalyst is studied in great detail after synthesis, but before being used, and after serving as catalyst for a certain amount of time. However, the additional information comes at the price of missing the evolution of the catalyst under working conditions.

From a practical point of view, it can also be useful to relate key descriptors, such as activity or selectivity, to parameters in the preparation of the catalytic material. In this approach, understanding has been pushed to the background: catalyst characterization has been replaced by testing for reactivity. This empirical way of developing catalysts has a strong trial-and-error nature. To successfully apply this approach, reactions are being run in parallel in great numbers, which allows the parameter space to be explored relatively quickly.

The drawback of the trial-and-error-based approach is that it may result in an improved catalyst, within the explored parameter ranges, but it cannot guarantee to find the best catalyst. In order to find the most efficient catalyst, the catalyst needs to be designed based on understanding, after which it may be optimized by following traditional approaches. To understand catalysis, we need to answer several key questions:

What is the atomic structure of the *working* catalyst, how does it adapt its structure depending on its environment? How does it evolve over time? If we know the active phase under reaction conditions, we can begin to understand its chemical interaction with the gas phase reactants. How do they adsorb, diffuse, and react on the catalyst? If we obtain this understanding on an atomic level, we can shift the focus to larger scale problems, such as diffusion, gas flow, and the thermal properties of the catalytic reactor.

1.3 In situ and operando experiments

Measuring interfacial properties of materials is inherently rather difficult, since the region of interest is only a few atomic layers thick and is frequently deeply buried by the phases that form the interface. For example, to study the solid-gas interface one needs to traverse the gas phases, without penetrating the bulk of the solid. This is rather straightforward if the gas is extremely dilute, such as a vacuum. However, catalysis does not occur in vacuum and to study it, the partial pressure of the reactants needs to be sufficiently high.

The main difficulty lies with the gas atoms that will disturb or completely inhibit most measurements that one would like to perform on the catalytically active interface. All surface-sensitive measurements involve particles, such as photons, electrons, ions, atoms or molecules, that are either impinging on the interface or originating from it. Most types of particle will not penetrate deep into a condensed phase, such as a solid, because their cross section for absorption or scattering is too large. This makes those techniques very surface sensitive. However, they have similar cross sections for interaction with gas molecules. If the gas phase layer is too thick or its pressure too high, then none of the particles will reach the interface or detector. If they do reach the detector via the interface, the information that they carry (momentum, energy, charge state, etc.) will be strongly deteriorated.

The usual strategy to overcome this problem (at least partly) is to make the gas phase layer as thin as possible. This can be achieved by moving the detector and/or source very close to the interface. A second solution is to construct a high-pressure cell with semitransparent windows that can be used within a vacuum chamber that houses the measurement instrumentation. Recent technical developments in surface science proved both strategies successful: X-ray photoelectron spectroscopy (XPS) measurements are possible at several mbars by moving the electron analyzer close to the surface, while focusing the X-ray beam to a small spot size [13]. The latter strategy is employed in high-pressure transmission electron microscopy (TEM), which uses high-pressure cells to image surfaces of catalytic nanoparticles under reaction conditions [14].

Another way to be less sensitive to the gas phase is to use high-energy photon techniques. For these techniques, the photon energy determines the interaction strength with atoms and molecules. For high-energy X-ray beams, these photons penetrate deeply into the solid phase and the surface information is entangled with bulk information. Several strategies can be adopted to increase the surface sensitivity. A general method to achieve this is to use a grazing-incidence angle. This increases the path length of the photons through the surface layers and decreases the probing depth. Some high-energy X-ray techniques are inherently surface sensitive, which is the case for surface X-ray diffraction (SXRD). The surface ends the extended periodicity of the bulk crystal and, therefore, changes the diffraction pattern [15]. Because all of these techniques have their limitations in both the conditions that can be probed as in the information that can be extracted, a combination of these techniques can be very powerful [16].

The in situ or operando measurements in this thesis are based on scanning tunneling microscopy (STM) [17], which is an example of scanning probe microscopy (SPM). These microscopes operate by sensing the interaction between surface atoms and a nanosharp probe. This probe is raster scanned in the region of interest, while the interaction is measured at every point. In STM measurements, this interaction is the tunneling current. In a typical measurement, the detector (the STM tip) is at a distance of $\sim$1.0 nm from the surface. The tip sample separation is much smaller than the mean free path of molecules in a gas phase (in the order of 100 nm at 1 bar at room temperature). This makes it possible to apply STM, in principle, almost irrespectively of the atmosphere, i.e., the choice of gas and the pressure. Actually, STM can be performed even in liquid environments and, with some care given to the tip and to the management of all potentials, even under electrochemical conditions [18].

The pressure insensitivity of SPM has been used to construct a dedicated high-pressure STM setup specialized to image solid, conductive surfaces under reaction conditions [19]. This unique system integrates the STM unit with a small high-pressure flow cell. The flow can consist of a mixture of up to 5 different gases in ratios that can be chosen over wide ranges and at a total pressure of up to 6 bar. This so-called ReactorSTM forms the current generation of a high-pressure STM concept, first described in our group by Rasmussen et al. in 1998 [20] and later refined by Hendriksen et al. [21] After almost 20 years of high-pressure STM experiments and technical development, this technique has become mature. This is illustrated by the STM experiments described in this thesis, which show true atomic resolution for the first time. Furthermore, true atomic resolution is achieved in almost every measurement. The latest developments include technical adjustments to the gas handling system that allow the absolute pressure to be increased to 20 bar. In addition, in the newest realization, the microscope can operate simultaneously in STM and atomic force microscopy (AFM) [22] mode. Combining STM and AFM has as major advantage that insulating surfaces can be imaged, while the current can be recorded as a function of the sample bias to obtain electronic information from the surface.

1.4 This thesis

In my PhD thesis, I will describe the experiments that I performed to (partially) answer the key questions mentioned at the end of section 1.2. To obtain fundamental knowledge on the elementary steps governing the catalytic process, I employed model catalysts. Model catalysts ideally capture the essence of the catalyst's activity, while greatly reducing the complexity of the system. In this way, I was able to study adsorption, reaction, and desorption in a precise manner. The model catalysts consisted of extended, flat versions of a metallic particle's surface. These model surfaces are created

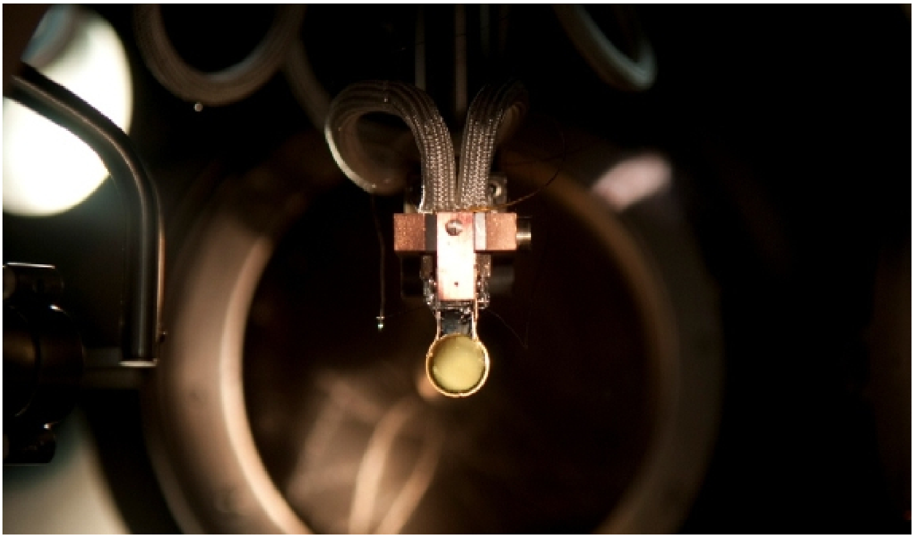

Figure 1.3: Au single crystal used as model catalyst. It was cut and polished to the (310) surface orientation. The crystal was mounted inside an ultra-high vacuum (UHV) chamber. Photograph by Leon Jacobse, M.Sc.

by cutting and polishing bulk single crystals in a specific orientation[2]. An example is shown in Figure 1.3. The precise orientation determines the arrangement of the atoms in the surface. The facets that define the shape of nanoparticles can be viewed as small regions with the structure of these flat surfaces and much of their properties can thus be derived from studies on the extended, flat surfaces. In my studies, I have found almost invariably that changes in reaction conditions, i.e., in temperature, in total pressure or in the ratio between the partial pressures of the reactants, can result in significant changes in the structure and composition, and, thus, the free energy of a surface. Precise knowledge of all these changes for all relevant surface orientations, would, in principle allow one to predict shape changes; a first and large step in understanding catalysis.

The first 3 chapters of this thesis focus on Pt, of which two model catalysts, the Pt(111) and the Pt(110) surface, were studied. In these experiments the ReactorSTM was used to obtain the atomic structure of these model catalysts under various reaction conditions. The first model catalyst, the Pt(111) surface, is the most stable Pt surface and should therefore be the dominant facet of Pt nanoparticles. Although the structure of this model catalyst is very straightforward and well studied[3], significant unclarity still exists about the way the surface oxidizes. Oxidation catalysis is an important application of Pt, thus justifying an in-depth study to elucidate the oxidation of the Pt(111) surface. This study is described in Chapter 2. In the following chapter,

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[2] These orientations are defined by their Miller indices, notated as (*hkl*) [23].

[3] One of the first papers using this Pt(111) model system dates back to 1969 [24] and over 3800 papers have been published since.

experiments are described that investigate the growth conditions of these surface oxides. Furthermore, the stability of these surface oxides was investigated by evacuating the reactor after forming the oxides. Finally, an estimate of the O coverage is obtained from XPS measurements performed under UHV conditions.

Chapter 4 presents a review dedicated to reactions on the Pt(110) surface. These reactions include CO oxidation and the reaction between NO and H_2. The CO oxidation experiments were performed by my predecessor, Dr. Kees T. Herbschleb. This review was published in a special edition of Catalysis Today, celebrating 50 years of research in heterogeneous catalysis at Leiden University [25, 26].

The second part of my PhD thesis follows a different approach. It describes a typical UHV surface-science study focused on low-temperature CO oxidation on a Au model catalyst. This field is much younger compared to CO oxidation on Pt and was started by Haruta et al. in 1987 [27]. They discovered an unusual and very high activity of Au nanoparticles for CO oxidation. One explanation for this reactivity is that Au nanoparticles deviate from the nobility of the bulk metal due to an increased number of low-coordinated atoms. Moreover, the addition of H_2O to the reactants was found to strongly enhance the activity [28]. In this project, I studied the interaction of water with low-coordinated Au atoms (see Chapter 5). In Chapter 6, I went one step further and created an activated water layer by electron-induced fragmentation and was able to follow the reaction of CO with O at very low temperatures.

The UHV surface-science study should be complemented at a later stage with an in situ or operando study to check if the metallic phase is indeed the active phase of these model systems. For Au, it is very realistic that the metallic phase is the stable phase under reaction conditions, since it is much more noble than Pt, of which only the top most layer oxidizes under reaction conditions.