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## Electrocatalysis at Single Nanoparticles

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# 1

## Introduction

### 1.1 On Catalysis

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Catalysis is vital to life on earth, and has been applied by mankind for ages; the leavening of bread requires yeast, as does the fermentation of beer and wine. Medieval chemists, or alchemists, knew how to fabricate a considerable catalog of substances, but they almost always required significant heating; they were baffled by the mysterious *vis vitalis* of organisms that performed chemical conversions at room temperature. In the nineteenth century, it was found that enzymes aid in these chemical conversions and that they can perform their catalysis even outside of living cells.

The discovery of the enzymatic concept was preceded by the discovery of the phenomenon of catalysis<sup>1</sup>, in the eighteenth century, when it was realized that otherwise stable gases reacted in the presence of specific metals. These experiments were performed by Joseph Priestley and later by Martinus van Marum, who reported the decomposition of ethanol vapours in the presence of various metals. The discovery of this phenomenon was quickly followed by its application, initially by sir Humphrey Davy as a lamp for English coal miners containing a platinum wire that would light up in the presence of flammable mine gas,[1] and later as the first lighter (a platinum catalyzed hydrogen flame) by Döbereiner.[2]

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<sup>1</sup>A wide range of substances, from enzymes, via soluble metal-organic complexes, to semiconductors are known to act as catalysts for chemical reactions. This thesis will however focus on the ability of pure metals to perform catalysis.

While the exact nature of these interactions was still poorly understood, the catalytic effect was already named in an early stage by Berzelius, who wrote a scientific review at the end of each year. He summarized the recent findings in catalytic experiments as follows: "It is, then, proved that several simple or compound bodies, soluble and insoluble, have the property of exercising on other bodies an action very different from chemical affinity. By means of this action they produce, in these bodies, decompositions of their elements and different recombinations of these same elements to which they remain indifferent." It was Berzelius who named this 'action' catalysis, but since he described it as a particular force (even using the term *vis occulta*) he did not contribute to the elucidation of the debate regarding the nature of the catalytic effect. Nevertheless, we still define a catalyst today as a substance that increases the rate of a chemical reaction, without being consumed in its process.

It follows from the above that catalytic research has always gone hand-in-hand with industrial application. At the present time, catalysis is an important industrial process that is employed from the conversion of crude oil into fuels to the detoxification of smoke-stack exhaust fumes. In fact, it is estimated that catalysts are used in 85-90% of the processes that generate bulk chemicals and materials.[3] Expressed in monetary terms, in 2012 the market for 'catalysis' alone is estimated at 20 billion dollars, a tiny amount considering its total output in the form of the petrochemical industry, which leans largely on catalyst enhanced productivity and weighs in at a staggering 2300 billion euros.[4] This implies that small gains in catalytic activity will lead to very large economic benefits. A subsection of the catalytic industry is electrochemical catalysis or electrocatalysis, in which case the catalyst increases the rate of a reaction that involves charge transfer. Electrocatalytic processes either supply electricity, or they require electricity for their functioning. Some electrocatalytic processes are operated on a very large industrial scale, such as the chlorine gas production, aluminium production and metal plating, and corrosion protection. In the production of chlorine gas (a very important bulk chemical) current is passed through two metal electrodes immersed in brine, yielding chlorine gas at the positive pole and hydrogen gas at the negative pole. The local production of chlorine gas by itself accounts for up to two percent of the Dutch electricity consumption.

Catalysts can be used to convert reactants into products, but they can also be used to convert fuels into energy more efficiently than conventional combustion. Recently, the potential to apply catalysts for energy uses has gained significant attention for several reasons. This is first of all due to rising fossil fuel prices, since catalytic conversion could make very efficient use of renewable hydrogen as a fuel. A second reason is

the increased demand for decentralized energy production as a balance to the recent increase in renewable energy, especially large fractions of which are solar and wind power that generate electricity intermittently.[5] Thirdly, increased use of hydrogen as a fuel would help abate the emission of carbon dioxide, which is recognized as a greenhouse gas. Catalytic fuel conversion could be combined with localized fuel generation providing large scale energy storage to reduce fluctuations in energy generation. An example of a catalytic fuel converter is the hydrogen fuel cell, which is the opposite of water electrolyzer cell. Two conductive poles are connected via an electronic circuit and a charge conducting electrolyte. Hydrogen is catalytically oxidized on one pole (the anode) sending protons through the membrane to the other pole (the cathode) where they recombine with the electrons transferred through the circuit in the oxygen reduction reaction (ORR). The electrons can do work in the circuit, meaning the fuel cell generates electricity.

The large-scale application of fuel cells is presently hindered by their cost, since expensive materials (at present mainly platinum) are necessary both for the catalysts performing the conversion of the fuel as well as for the sophisticated membranes that must conduct protons whilst remaining impenetrable to fuel. To reduce the amount of scarce metals in a fuel cell, their catalytic efficiency must be maximized. The major source of inefficiency is the oxygen reduction reaction at the fuel cell cathode. Over the last decades, research into increasing the efficiency of the catalyst by many groups worldwide has led to significant cost reduction.[6] To appreciate and discuss details on the state of the art of fuel cell catalysis, it is necessary to take a jump back in time.

## 1.2 From surface science to nanoparticle studies

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Fundamental studies of the reactions that occur in fuel cells go back at least 200 years. The eminent Michael Faraday was working closely with Humphrey Davy and had reproduced the experiments of Döbereiner personally. In 1834, he reported that the catalytic reaction could only occur at the metal surface, since the (catalytic) oxidation of hydrogen on a Pt plate was greatly diminished by fouled surfaces,[7] however throughout the nineteenth century there was a debate on the exact nature of these catalytic interactions.[8] Irvin Langmuir, some 80 years later, expanded on the understanding of reactions at surfaces with more quantitative studies on the nature of adsorbing and dissociating gas molecules.[9] Studies on the nature of the interaction between molecules and metal surfaces benefited greatly from technological development, specifically the generation of ever higher vacuums and the controlled manufacture of single crystalline

metals of very high purity, polished to mono-atomically flat surfaces. These developments enabled very clean, model measurements, performed using a variety of probe techniques.[10]

It was found from these studies that catalytic reactions are highly sensitive to the local arrangement of metal atoms in the surface. A metal surface is a truncation of an infinite crystalline lattice, and the orientation of the plane intersecting that lattice determines the two-dimensional arrangement of the atoms in the surface. A crystal that is cut on all sides is shown in Figure 1.1, revealing the different atomic configurations. Upon cleaving the lattice, the atoms in the surface lose the electronic interaction with the layer previously above them, changing the local electronic properties of the surface atoms. With respect to the bulk structure, the atoms in the surface become under-coordinated. The coordination of the metal atoms is further reduced, when the amount of neighbouring atoms in the plane goes down, the degree of which is dependent on the truncation plane of the crystal. The possible planes of truncation are indicated by the so-called Miller index notation (hkl), and are orthogonal to the vector on the axes of the lattice element (the unit cell, that is propagated infinitely in three dimensions to form the crystal) indicated by the Miller index numbers. For the face-centered cubic crystal structure of most metals, three elementary truncations form the basal planes and these are referred to as (111), (110) and (100) surfaces. The (111) surface is the most stable surface with the highest coordination, while the (110) surface has the lowest coordination.[11] When the crystal is truncated at an angle that does not perfectly correspond to a basal plane, a staircase-like surface is revealed that follows the angle of the cut. Such surfaces thus include steps – which separate longer terraces in a basal plane orientation – that are also under-coordinated.

These single crystal surfaces started to be applied to electrochemical measurements as well, with important work done by Clavilier.[12, 13] Surface sensitivity in electrocatalytic reactions was also revealed, with very clear dependence on the surface structure for the oxidation of carbon monoxide on Pt electrodes.[14] It was found that Pt (111) surfaces have the lowest activity for the CO oxidation, and that the introduction of steps leads to a significant increase in the reactivity. The steps can have either a (110) or a (100) orientation, and both step sites are more active than the (111) plane for the CO oxidation.[15] It was suggested that the oxygen species required for CO oxidation adsorbs preferably at the step sites and that the reaction between CO molecules and oxygen atoms occurs only there.[16]

The model studies that followed from the work of Faraday and Langmuir have resulted in a tremendous increase in insight. They were however always complimented

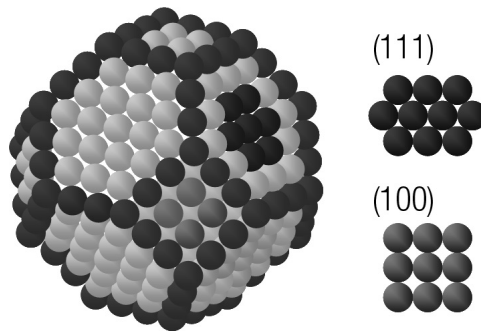


Figure 1.1: A cubo-octahedral nanoparticle; the triangular and diamond faces are the (111) and (100) orientation respectively, while the edges are highlighted for clarity.

by applied catalytic studies in which libraries of materials were screened for catalytic activity. Such techniques have been very successful in industrial practice, and it was in this way that the catalyst for ammonium synthesis in the famous Haber-Bosch process was developed. Industrial catalysts are prepared with a very high surface area to weight ratio, in order to reduce the cost incurred by metallic 'dead weight', especially relevant when considering the scarcity of some of the metals used in applied catalysis. The increase in surface area is achieved by using fine metal particles that are called nanoparticles when they reach a diameter smaller than 100 nm. Presently, the fields of model surface science-type measurements and catalytic screening measurements are converging as model surface reactions are being analyzed under reaction conditions[17, 18] and nanoparticle ensembles can be followed using in-situ techniques[19] and high resolution electron microscopy.[20]

It has been observed that the catalytic activity of nanoparticles is related to their size and shape, which is attributed to the change in atomic configuration of a nanoparticle of ever-decreasing size.[14] A nanoparticle is in its most stable shape when the contribution of low energy basal planes (the (111) and (100) planes in the case of Pt) to the surface is maximized. Therefore, particles tend to take a cubo-octahedral shape of which the fractions of (100), (111) as well as edge sites can be calculated for any NP radius, as shown in Figure 1.1.[21] In this way, results obtained on single crystal model surfaces can be correlated with those obtained for nanoparticles of increasing radius. For the CO oxidation reaction one would expect, from the behaviour observed on single-crystal electrodes, an increase in activity for smaller particles containing a large fraction of edge sites. On the contrary it was found that small particles have a lower activity for the CO oxidation than large particles.[22] As particles increase, the basal planes start to show defects and these sites have been suggested to be most

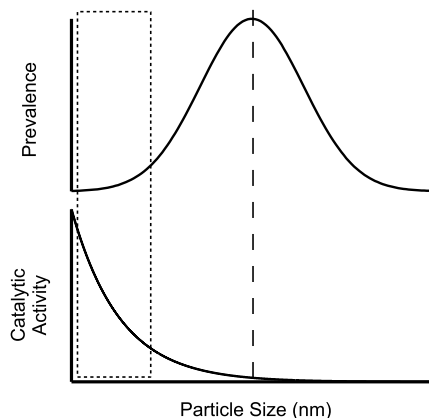


Figure 1.2: Schematic; when the catalytic activity of nanoparticles does not depend linearly on their size, no accurate size dependence can be obtained from ensemble measurements using the mean NP size.

active.[23] This indicates that the nature of particle edges and step sites on extended surfaces is quite different.

### 1.3 Nanoparticles; the contents of this thesis

The particle size effect for the CO oxidation has been found by studying large ensembles of NPs, placed on planar electrodes or porous carbon supports. The catalytic activity measured in this way is related to the average particle size obtained through e.g. transmission electron microscopy (TEM) measurement of a NP sample. The NP size is usually distributed normally around a mean value, which is taken as the average size when reporting the catalytic measurements. Nevertheless, as indicated in Figure 1.2, the NPs at the ends of the distribution may have very much altered reactivity, certainly in reactions that have a non-linear dependence on the particle size, as has been reported for the CO oxidation. Moreover, since not all particles of equal size must also have an equal shape, the translation between activity and size may not be so straightforward. It is therefore interesting to specifically study the activity of individual particles, preferably if they have well-defined shapes and sizes.

An additional topic related to the study of applied fuel cell catalysts, is the influence of the interaction between particles on the catalytic activity. Since NPs consume reactant from the electrolyte around them, they locally induce a concentration gradient that extends a certain length into the electrolyte. The typical distance influenced by



the concentration gradient is called the diffusion length, and it may be large enough to perturb mass transport towards an adjacent particle, thereby reducing the flux of reactant arriving at two interacting nanoparticles. The study of individual particles and well controlled ensembles of nanoparticles has received a considerable amount of reports in the very recent literature, to be discussed in greater detail in the second chapter of this thesis.

Experimental results obtained for the study of individual nanoparticles and the interaction between discrete amounts of particles are also included in this thesis. These are separated in two distinct methods of studying single catalyst NPs, as depicted in Figure 1.3. One way to monitor the signal from a single particle is to create a very tiny 'landing platform' of an electrode, which has as its only function to conduct electrons to or from the catalyst particle, without generating a large signal of its own. This means that such an electrode must be small enough to prevent the generation of significant current and the material that it is made out of should be catalytically inert, that is, unable to catalyze the same reaction as the catalyst particle under study. The maximum size of the electrode is determined by its background current, and is on the micrometer scale.

Reaching such electrode surface areas using conventional mechanical electrode preparation is increasingly difficult; therefore the microscopic electrodes used in this thesis are fabricated using (nano-)lithography. The characterization of lithographically fabricated electrodes is discussed in chapter 3, while details of the fabrication process can be found in appendix A. In this chapter it is shown that by using lithographical fabrication, very small nanoelectrodes can be made reproducibly and that they can be reliably characterized using both electrochemical measurements and scanning electron microscopy. After a confined area is successfully designated to be used for electrocatalytic measurement, NPs should be immobilized on the electrode surface. A very controlled way of depositing NPs on an electrode surface is to inject NPs into the electrolyte and monitoring electrochemical signal due to their arrival at the electrode. For example, one can observe the step-wise extinction of a redox current running at an electrode being covered by the cumulative landing of insulating particles.[24] A particularly powerful way of detecting the arrival of catalyst particles is through their electrocatalytic conversion of a substrate in solution that is not converted at the support electrode. This method was pioneered in the research group of A.J. Bard, by showing the detection of individual Pt NPs on a carbon ultramicroelectrode (UME) that was held at the potential of the hydrogen evolution reaction on Pt. Consequently, a step-wise increase in the cathodic current was observed at the electrode.[25] In chapter 4 a sim-

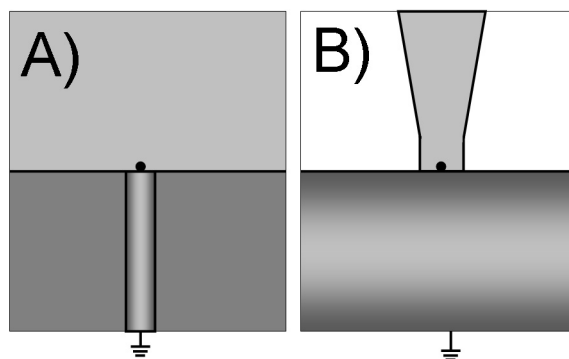


Figure 1.3: Two ways to study the activity of a single catalyst particle electrochemically: A) using a small electrode submerged in a quasi-infinite volume of electrolyte or, B) a quasi-infinite planar electrode with a confining electrolyte.

ilar experiment is used to detect the arrival of individual Pt NPs at a lithographically fabricated Au UME. We discuss in this chapter the necessity for careful characterization of the electrode after detecting the arrival of NPs. Specifically, complications for this detection mechanism regarding the aggregation of Pt NPs in solution by the electrocatalytic substrate are discussed.

An alternative manner to measure an individual catalyst particle on a very small electrode area is to confine the amount of electrolyte in contact with its surface, as shown in panel B) of figure 1.3. Such conditions are met if a very tiny electrolyte droplet is placed onto a surface. When an electrolyte-filled pipet with a very narrow taper (so that its tip is one micron across or smaller) contacts an electrode surface with the meniscus formed at its end, the electrolyte boundaries on the surface are microscopic. Reference electrodes can then be introduced inside the pipet so that electrochemical measurements can be performed against (a section of) the electrode. Using pipette tips contacting TEM substrates allowed the characterization of individual particles both electrochemically and microscopically as shown in chapter 5. Importantly, cyclic voltammograms measured at a single Au NP, which was also analyzed using TEM, are reported.

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