

**The structure of a working catalyst ; from flat surfaces to nanoparticles** Roobol, S.B.

#### Citation

Roobol, S. B. (2014, December 2). *The structure of a working catalyst ; from flat surfaces to nanoparticles*. Retrieved from https://hdl.handle.net/1887/29891

Version:Not Applicable (or Unknown)License:Leiden University Non-exclusive licenseDownloaded from:https://hdl.handle.net/1887/29891

**Note:** To cite this publication please use the final published version (if applicable).

Cover Page



## Universiteit Leiden



The handle <u>http://hdl.handle.net/1887/29891</u> holds various files of this Leiden University dissertation

Author: Roobol, Sander Bas Title: The structure of a working catalyst : from flat surfaces to nanoparticles Issue Date: 2014-12-02

# Chapter 1 Introduction

Surface science and heterogeneous catalysis are a natural match, and this thesis further strengthens this alliance. In both fields, the interaction of molecules with solids forms a central topic. Although the two fields are complementary, as they approach this topic from two different sides, it is usually difficult to directly relate results obtained in one field to results obtained in the other. Bridging this gap has been a driving force for the work described in this thesis.

Traditional catalysis research can be seen as taking a top-down approach. Understanding is derived from ensemble measurements on the reactants and products, e.g. the catalyst activity (how much reactant is converted) and selectivity (how much of the desired product is formed compared to undesired byproducts). This is often combined with extensive catalyst characterisation before and after reaction, using spectroscopy and microscopy. The challenge of this approach is usually in the catalytic system itself, for example because there are several competing reactions, or because the catalyst has a complex composition or structure. The gain is relevant knowledge for applications in e.g. the chemical industry, but the knowledge is often phenomenological in character.

Catalytic surface science takes a bottom-up approach and uses highly simplified model systems under minutely controlled conditions. A typical surface-science experiment studies a flat single crystal metal surface, often during interaction with molecules, in Ultrahigh Vacuum (UHV), and often at cryogenic temperatures. The difficulty of such experiments is to exert near-perfect control over the sample, and at the same time apply highly sensitive and often very delicate measurement techniques. When succeeding in both, the experiment gives information on the atomic scale, e.g. on the chemical state or the atomic structure of the surface or the adsorbates.

#### The pressure gap and the materials gap

In practice, it is often difficult to relate results obtained by the traditional chemical approach to results obtained by surface science techniques. There are only a few documented cases in which the activity and selectivity of a real catalyst under realistic conditions can be predicted even to within one order of magnitude, based on the extrapolation of surface-science experiments[1, 2]. This suggests that there are intrinsic qualitative differences, for example in the reaction mechanisms, that are introduced when the experimental conditions differ too much. The two fields are often said to be separated by two gaps, the *pressure gap* and the *materials gap*. This thesis describes work done in the field of *in-situ* catalysis, in which we have aimed to overcome these gaps and combine the atomic-scale sensitivity of surface science with the relevant conditions of traditional catalysis research.

The *pressure gap* refers to the difference in operating pressure and temperature between applied catalysis and traditional surface science. In the chemical industry, catalysis typically takes place at pressures in the range of 1-100 bar and temperatures up to 1000 K[3]. Classical surface science uses low pressures in the range of  $10^{-10}$  to  $10^{-6}$  mbar, and a wide range of temperatures, down to a few K and beyond 1000 K[4]. A naïve justification to extrapolate surface science results to real catalysis would be to use thermodynamics to argue that the conditions can be chosen such that the chemical potentials of the involved species are the same in certain low-pressure, low-temperature conditions as they are in the real high-pressure, high-temperature conditions. However, real catalytic processes are never in thermodynamic equilibrium and the role of kinetics must be taken into account. The kinetics strongly depend on temperature, and the enormous difference in kinetic limitations between high and low temperature are the cause of the *pressure gap*. These kinetic limitations could be either on the catalyst surface (e.g. due to barriers for diffusion, adsorption/desorption or reaction steps) or in the gas phase (where not only diffusion but also fluid dynamics needs to be considered).

It is important to realise that it is not enough to operate at high pressure and high temperature to fully overcome the *pressure gap*. This only gives representative kinetics on the catalyst surface, given a certain chemical potential for the relevant gas species. But the composition of the gas phase, and thus the chemical potential, is not necessarily representative. To reach true catalytic conditions, the activity of the catalyst needs to be representative as well, not only when expressed in converted molecules per site per second, but also when expressed in terms of the (local) partial pressures of the products and reactants. This means that the reactor volume and the residence time of the gas in the reactor need to be matched to the catalyst activity and surface area, and for a surface-science experiment this typically means that the reactor volume needs to be minimised. Only then, the true interplay between catalyst structure and reactivity can be studied. This interplay goes both ways: the reactants and the products affect the catalyst structure, but the catalyst structure influences the activity and thus the presence of reactants and products[5].

The *materials gap* is due to the difference in complexity of catalysts between industrial catalysis and traditional surface science. Real, commercial catalysts are typically multi-scale materials, e.g. metal nanoparticles, dispersed on a threedimensional, porous oxide support, pressed into centimetre-sized pellets. The flat metal surfaces used in surface science are easier to understand, but lack many of the features of a real catalyst. For example, nanoparticles have a much larger variety of adsorption sites than extended flat single-crystal surfaces[6] and they can have a different electronic structure from the bulk material[7]. Additional effects arise from the interaction between the metal particle and the support, e.g. via spillover effects[8] or further changes in the electronic structure[9].

#### New instrumentation to bridge the gaps

New instrumentation is needed to bridge the *pressure gap* and the *materials gap* and combine the best of both approaches. The ambition is to combine the atomic-scale sensitivity from surface science with the applicability and relevance of traditional catalysis research. In other words, to obtain information on the fundamental atomic-scale mechanisms that are actually at play in a real catalyst under real conditions. The first part of this thesis is dedicated to the development of new instrumentation for this purpose.

Several *in-situ* techniques are already available, some of which have been developed very recently. These include Scanning Tunneling Microscopy (STM)[10, 11], Transmission Electron Microscopy (TEM)[12, 13], several hard X-ray scattering techniques[14, 15], several variants of X-ray absorption spectroscopy[16], X-ray Photoelectron Spectroscopy (XPS)[17], and infrared spectroscopy[18]. Preferably, these techniques should be used simultaneously with traditional chemical techniques such as mass spectrometry and calorimetry. In addition to these experimental techniques, theoretical approaches such as the combination of Density Functional Theory (DFT)[19] with Kinetic Monte-Carlo[20] and fluid dynamics simulations[21] can be also considered to bridge the *pressure gap*.

This thesis takes a multi-technique approach to *in-situ* catalysis research. We have applied new and existing *in-situ* measurement techniques to study the fundamentals of several catalytic reactions. The latest technique is Atomic Force Microscopy (AFM), for which we have built a novel instrument with unique capabilities. The other *in-situ* techniques that we have applied are TEM and three X-ray scattering techniques: X-Ray Diffraction (XRD), Surface X-ray Diffraction (SXRD) and Grazing Incidence Small Angle X-ray Scattering (GISAXS).

The first part of this thesis describes the development of new instrumentation

for *in-situ* catalysis in all its aspects: mechanical hardware, electronic hardware, and software. A major part of this is devoted to the ReactorAFM that we have developed as part of this thesis work. The ReactorAFM is the world's first high-pressure, high-temperature Non-Contact AFM.

Chapter 2 describes in detail the design and performance of this instrument. In short, the ReactorAFM can image model catalysts, not only flat surfaces but also supported nanoparticles, at temperatures up to 600 K and pressures up to 6 bar, with a resolution in the order of a nanometre. The instrument consists of a 0.5 ml high-pressure flow reactor joined with an AFM scanner based on a quartz tuning fork. The reactor/scanner is located in an ultrahigh vacuum system to be able to use standard surface-science techniques to prepare and characterise the sample. The true value of the ReactorAFM is demonstrated in chapter 7, where it provides an essential element in a combined study with three other *in-situ* techniques, showing that it can bridge both the *pressure gap* and the *materials gap* while providing information on the atomic scale.

In the context of instrumentation development for complex experiments, new hardware cannot be seen separately from specialised software, in order to deal with the increasing complexity of the generated data. Chapter 3 introduces *Spacetime*, a user-friendly data browser for *in-situ* experiments. During *in-situ* microscopy studies, a variety of signals is recorded in addition to the images, for example the sample temperature, the gas flow settings and the output of a mass spectrometer. These signals are typically recorded independently from the microscopy data, often on separate computers, by a variety of software packages, ranging from home-built LabVIEW programs to professionally designed, commercial applications. *Spacetime* can provide an integrated overview of the heterogeneous datasets obtained during *in-situ* experiments, and has now become an essential tool in our laboratory.

A second software package is described in chapter 4. Thanks to recent developments in the field of SXRD, the data acquisition rate has increased tremendously. We have developed *BINoculars* as a tool for the reduction and analysis of large datasets obtained by a two-dimensional X-ray detector. When operating at a modern diffraction beamline and with access to a computing cluster, it allows the acquisition and processing of large-area, high-resolution reciprocal space intensity maps on a time scale of tens of minutes. It is already considered part of the basic toolkit by the staff of the ID03 beamline at the ESRF and it has received interest from several recurring users.

#### Operando catalysis

The second part of this thesis concerns studies on relevant catalytic model systems with several *in-situ* or *operando* techniques.

We start with two studies on the reduction of nitric oxide (NO) by hydrogen  $(H_2)$  using a platinum catalyst. This system can be seen as a model reaction for the reduction of NO that takes place in the three-way car catalyst. Since no literature was available on high-pressure surface-science experiments on this reaction, we started with a flat single crystal surface. In chapter 5, SXRD is used to study the interaction of mixtures of  $H_2$  and NO with a Pt(110) surface at 1 bar and 100-400°C. This surface orientation of Pt easily reconstructs, and we have observed several new reconstructions under high-pressure conditions. In addition, after prolonged exposure to NO/H<sub>2</sub> mixtures, the flat surface started faceting into vicinal orientations close to the (320) orientation. As many catalytic reactions take place predominantly on step sites, it is extremely relevant to understand when and how a catalyst might be actively forming steps. In this case, we suggest that the mechanism for the step formation is related to the surface stress of the Pt(110) surface, which is dramatically altered by the high coverage of adsorbed NO molecules due to their repulsive interaction. This demonstrates that high-pressure restructuring mechanisms can not exclusively be interpreted or predicted on the basis of adsorption energies at different sites, but also the surface stress needs to be considered. This is a true pressure gap effect: the high NO coverage, combined with sufficient mobility of the metal atoms on the surface to reorder on this scale, can only be obtained under high-temperature, high-pressure conditions.

Having seen this mechanism on flat surfaces, it is natural to wonder what this means for a more realistic catalyst, i.e. a system of metal nanoparticles. This is the topic of chapter 6, where we used TEM in combination with nanoreactors, specially designed for *in-situ* catalysis studies[13]. In general, the shape of a nanoparticle is dictated by the relative free energies of all interfaces between the particle and the gas environment. We observed that initially faceted particles became more rounded under the influence of NO, i.e. the flat, low-index facets broke up into vicinal surfaces. Thanks to the measurements on the flat (110) surface in the previous chapter, we can now understand that this is the logical nanoparticle analogue of the same mechanism: adsorbate-induced stress is held responsible for the change in surface free energies.

For the last chapter, we took on the archetypical model system of CO oxidation on palladium, but brought it to the next level by bridging the *materials gap*. This study builds on the vast amount of surface-science knowledge, both at low- and at high-pressure, that is already available for CO oxidation catalysed by palladium surfaces. In addition, CO oxidation at high pressures is a great example to show the defining difference between high-pressure surface science and *in-situ* catalysis. The reason for this is the existence of a diffusion-limited high-reactivity regime, which is accompanied by large gradients in the CO partial pressure. This shows that aspects such as reactor design cannot be neglected. High-pressure surface science can be used to study surface structures, but the relevance for catalysis needs to be established from a surface-sensitive, *in-situ* catalytic measurement.

Apart from taking a true *in-situ* approach to bridge the pressure gap, chapter 7 also bridges the *materials gap*, by moving beyond flat surfaces to a supported nanoparticle model system. Using size-selected Pd particles on a  $Al_2O_3$  substrate, we observed reaction oscillations: at constant conditions (external heating power and gas feed), the system periodically switches between a high-reactivity regime and a low-reactivity regime. Here, our multi-technique approach really shows its power: by combining XRD, GISAXS, AFM and TEM, all *in-situ* during high-temperature, high-pressure reaction conditions, we have resolved a key ingredient of the mechanism of the reaction oscillations by establishing the presence of a 1 nm thin oxide shell, which is only present during the high-reactivity part of the oscillation period.

### A multi-technique approach

The multi-technique approach to *in-situ* catalysis, as advocated in this thesis, is imperative. There is no single *in-situ* technique that can tackle all aspects of even the simplest catalytic reactions.

By combining several *in-situ* techniques, we can gain detailed understanding not only of archetypal model reactions like CO oxidation, but also of more complex catalytic systems.