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Onderwaater, W.G.

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Willem George Onderwaater
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Promotor:
Prof. dr. J. W. M. Frenken
Universiteit Leiden
Co-promotor:
Dr. R. Felici
CNR, Rome, Italië

Promotiecommissie:
Prof. dr. E. R. Eliel
Universiteit Leiden
Prof. dr. J. M. van Ruitenbeek
Universiteit Leiden
Prof. dr. F. M. F. de Groot
Universiteit Utrecht
Prof. dr. E. Lundgren
Lund University, Lund, Zweden
Dr. I. M. N. Groot
Universiteit Leiden
Dr. M. J. A. de Dood
Universiteit Leiden
Dr. G. Renaud
CEA, Grenoble, Frankrijk

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aan mijn ouders

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Preface

The use of catalysts has become an essential part in many industrial production processes. Exerting control over chemical reactions with the help of catalysts is an important aspect of our chemical industry. From the petrochemical to the pharmaceutical industry and in the production of many materials, catalysts are widely used to create the chemicals society relies upon. In order to expand and refine the application and usefulness of catalysis, a detailed, atomic-scale understanding of all aspects of catalytic reactions is fundamental.

The oxidation of CO forms a popular model system for heterogeneous catalysis. In this reaction, two types of molecules, carbon monoxide and oxygen, adsorb on the catalyst surface. Upon adsorption, each oxygen molecule dissociates into two atoms. When a carbon monoxide molecule and an oxygen atom meet, they can react to form carbon dioxide, which desorbs after the reaction. The task of the catalyst is to bring together the reactants and possibly lower the barrier for formation of the product. In this way, the effective activation energy of the reaction is reduced, which lowers the temperature at which the reaction can take place. This is one of the general roles of a catalyst. In addition to making the reaction conditions more favourable, catalysts are also developed to improve the selectivity of desired products over side products.

The basic mechanism of even a simple, heterogeneous catalytic reaction, such as CO oxidation, involves a wide variety of physical and chemical concepts. These range from basic considerations of the atomic-scale structure of the catalyst's surface and its interactions with the reactant molecules to the large-scale architecture of the catalyst itself and the reactor vessel in which the chemistry is to take place. Each of these individual elements forms an important research field in itself. In addition, understanding the interplay between all these aspects forms a formidable challenge of catalysis.

Let us inspect a few of the elementary reaction steps in more detail by considering a catalytic process at a modest pressure of 1 atmosphere and a modest temperature, namely room temperature. Under these conditions, every active atom on the catalyst surface is visited approximately every nanosecond by a reactant molecule from the gas phase. If the molecule adsorbs, its location on the surface may not be its last resting place. The molecule may diffuse over the surface to other, possibly more favourable locations. The molecule can dissociate upon adsorption. It can dissolve and travel into the bulk. The dissociated molecule can chemically engage with the catalyst to form a new chemical compound together with catalyst atoms. Reactant molecules that are attached to the surface, can execute a chemical reaction with each other. In many cases, more than a single reaction pathway is available, leading to more than a single possible type of product molecule. If the catalyst functions properly, the product molecules will desorb from the surface and make place for new reactants to adsorb.

Which of the reaction pathways is followed, depends on the energy landscape of the reaction, i.e. the total potential energy of the combination of the catalyst and the molecule or molecules that reside on it as a function of all spatial coordinates of the atoms of the catalyst and the molecules involved. The shape of this energy landscape depends on the chemical and physical characteristics of the relevant molecules and the catalyst and their interaction. It contains all the details of the Van der Waals type interactions that the molecules experience at a large distance from the catalyst and the electronic interactions that lead to the possible binding and dissociation of the molecules at close distance. This landscape is a very-high-dimensional potential energy surface, in which many parameters can be relevant, such as the precise position and orientation of each molecule, the internal deformations of the molecules and the detailed rearrangements of the catalyst surface, in response to the presence of the adsorbate. As such, it contains all information on energy barriers for diffusion, dissociation, reaction, desorption and all other processes that the molecule-catalyst system can engage in.

It may be clear from this introduction that catalysis is typically so complex that no single experiment can reveal all relevant details of a reaction, for example finding the reaction pathways, the precise geometrical configurations, the corresponding electronic rearrangements and the energy barriers that are involved in each of the reaction steps. In practice, one has to combine a multitude of information obtained with various experimental techniques, in order to unravel a catalytic reaction. Usually, microscopy is required to identify bonding geometries, often under conditions that are remote from real reaction conditions, spectroscopic techniques are employed to acquire information about the electronic and chemical bonding characteristics of reactants, intermediate products and final products, and dynamic, temperature-dependent measurements are used to measure rates, binding energies and energy barriers.

Theoretical predictions of the potential energy surface are often obtained with the use of Density Functional Theory (DFT). In view of the enormous complexity of the energy landscapes of even the simplest reactions, usually these calculations are restricted to very limited ranges of configurations and reaction pathways. Combining the total-energy calculations with the thermodynamic contributions from the reactants in the gas phase, one can construct the more relevant free-energy landscape, with the most probable surface and adsorption geometries. Additional calculations are then still required to determine energy barriers and model the kinetics of a catalytic process, which is necessary to establish to what extent the reactions define a dynamic equilibrium configuration that deviates from the thermodynamic equilibrium structure.

The catalyst can take a variety of shapes. For fundamental research studies, usually simple shapes are used, such as that of a flat, single-crystal surface. Practical catalysts, such as in the car catalyst or in most industrial processes, often take the form of an ensemble of nanoparticles. Usually, these are residing on a support structure, such as an oxide or a zeolite. On a larger scale, the catalyst material is often shaped in the form of pellets. On a macroscopic, industrial scale, these pellets are loaded into a reactor vessel. This hierarchy of length scales and materials brings in additional elements of complexity in the behaviour of catalysts. For example, the geometry of the reactor and the material loaded into it, will influence the flow pattern of the reactants and products, the distribution of the composition of this flow, and the temperature distribution. In turn, all of these parameters may influence the local state of the catalyst, the local reaction mechanism and the local reaction rate and these can all vary from one side of the reactor to the other.

Even though some of the basic catalytic mechanisms may be unraveled in great detail under laboratory conditions that are very remote from actual reaction conditions, in particular under low pressures or even ultrahigh vacuum, it is essential that sensitive experiments are also conducted with a variety of techniques at elevated temperatures and elevated gas pressures. To this end, the last decade has seen an enormous effort to develop new equipment for catalysis research. Techniques like Transmission Electron Microscopy (TEM), Surface X-ray Diffraction (SXRD), Scanning Tunneling Microscopy (STM), Atomic Force Microscopy (AFM) and X-ray Photoelectron Spectroscopy (XPS) have been successfully adapted to study catalysis at high pressures. Part of the present PhD thesis is devoted to such developments. Chapters 1 and 2 present two new setups to investigate catalytic reactions. In chapter 1 we present a setup that combines SPM with SXRD. Both techniques are able to resolve features at a length of Ångströms. With the combination of a scanning probe technique and a diffraction technique we aim to couple structural information on the surface over length scales ranging from atoms to micrometres. To investigate the behaviour of the catalyst at millimetre length scales we present a simple optical technique in chapter 2. This technique monitors the optical response of a flat catalyst with 1 centimetre diameter during a reaction. At this length scale the influence on the surface composition and roughness due to variations and gradients in the composition of the gas phase becomes visible.

To make optimal use of the available techniques we have developed new software to combine, reduce and analyse large volumes of x-ray data. Chapter 3 presents the analysis program BINoculars for SXRD data. This software package allows one to handle and combine large amounts of data from a surface diffraction beamline and to analyse these in a convenient and natural way.

Spontaneous reaction oscillations are one of the manifestations of complex behaviour that can result from the collective interplay of different aspects of a catalytic reaction. In chapter 4 we investigate reaction oscillations in the CO oxidation reaction on a palladium(100) surface. Intervals of high surface reactivity are periodically followed by an intervals of low reactivity. This oscillatory behaviour results from interaction between the surface reactivity and the gradients of the CO partial pressure in the reactor. We analyse in detail the structure and morphology of the catalyst surface in order to investigate the origin of the specific oscillation characteristics. A possible ingredient of the oscillation is the distribution of length scales of surface roughness that can form during the intervals with high reactivity. This concept is explored further in chapter 5 where we calculate if the observations of chapter 4 can be explained by the evolution of the roughness characteristics.

By changing from a single-crystal catalyst to a nanoparticle system in chapter 6, we attempt to study catalysts in an in a geometry that is closer to what is used in practical applications. The technological step required to analyse nanoparticles as opposed to single-crystal surfaces is considerable. Dedicated experimental tools to analyse nanoparticles under operating conditions, like in situ TEM, have become available only recently. We use three experimental tools, TEM, STM and SXRD, to investigate how palladium nanoparticles change shape during the oxidation of CO.