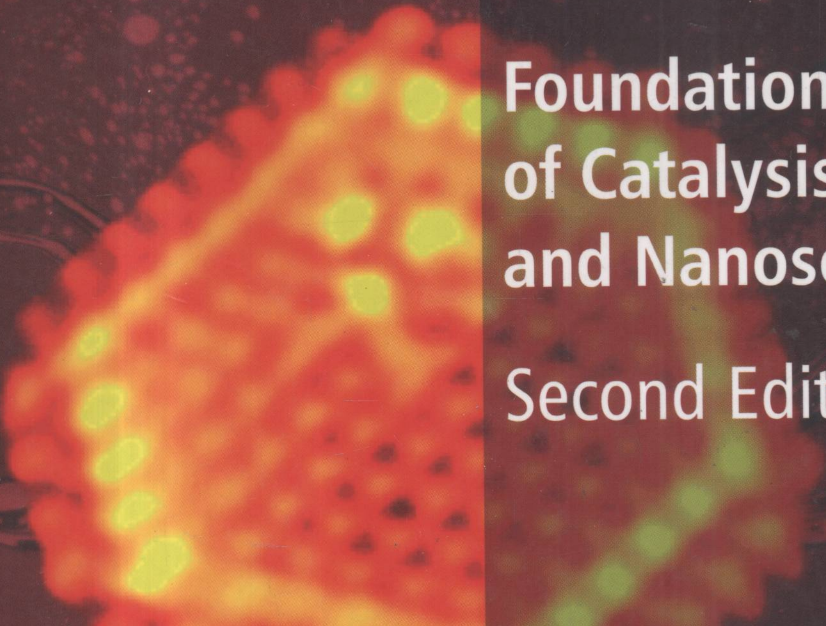
SURFACE SCIENCE



Foundations of Catalysis and Nanoscience

Second Edition

Kurt W. Kolasinsk

WILEY

Surface Science: Foundations of Catalysis and Nanoscience

Second Edition

DR KURT W. KOLASINSKI
Department of Chemistry, West Chester University, West Chester, PA, USA

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2007 was a great year for surface science as celebrated by the awarding of the Nobel Prize in Chemistry to Gerhard Ertl "for his studies of chemical processes on solid surface". I was fortunate enough to work in Ertl's *Abteilung* in Berlin and to see how he helped build the surface science approach. While it was Irving Langmuir's work that established the basis for understanding surface reactivity, it was not until the work of Gerhard Ertl that surface chemistry emerged from its black box and that we were able to understand the dynamics of surface reactions on a truly molecular level.

There comes a time about a year or so into working on a textbook when every author has a David Byrne moment, asks him or her self "My god!... what have I done?" and wonders how he is going to finish the task. It has been a great pleasure to hear from so many students that they found the first edition of this book so informative and readable, and it is from them that I have derived the great motivation for writing this second edition. I also thank the many individuals who have pointed out errors in the first edition including Scott Anderson, Eric Borguet, Maggie Dudley, Laura Ford, Soon-Ku Hong, Weixin Huang, Bruce Koel, Lynne Koker, David Mills and Pat Thiel as well as David Benoit, George Darling, Kristy DeWitt and David Mills for help with answers to and data for exercises. A special thanks to Eckart Hasselbrink for a critical reading of Chapter 8 and to Maggie Dudley for her persistence in casting a critical eye on several sections. I would particularly like to acknowledge Flemming Besenbacher, Pallab Bhattacharya, Mike Bowker, George Darling, Istvan Daruka, Gerhard Ertl, Andrew Hodgson, Jonas Johansson, Tim Jones, Jeppe Lauritsen, Volker Lehmann, Peter Maitlis, Hari Manoharan, Katrien Marent, Zetian Mi, TC Shen, Joseph Stroscio, Hajime Takano, Sachiko Usui, Brigitte Vbgele, David Walton and Anja Wellner for providing original figures. The heroic efforts of Yukio Ogata in securing the *sutni nagashi* images were remarkable. Finally, perhaps because I cannot end without some nod to history and the long road to the second edition, a passage from Czesiaw Mitosz: "Durch die Entfernung werde ich dazu verleitet, in meiner Phantasie eine Heimat zu erschaffen, die in der Geschichte liegt. Wo immer ich mich auf der Erde bewege, trage ich sie mit mir wie die Schnecke ihr Haus."

Kurt W Kolasinski
West Chester
February 2008

Contents

Surface Science: Fundamentals of Catalysis and Nanoscience

Introduction

When I was an undergraduate in Pittsburgh determined to learn about surface science, John Yates pushed a copy of Robert and McKee's *Chemistry of the Metal-Gas Interface*[1] into my hands and said 'Read this'. It was very good advice and this book remains a good starting point for surface chemistry. But since the early 1980s, the field of surface science has changed dramatically. With the discovery by Binnig and Rohrer[2,3] of the scanning tunnelling microscope (STM) in 1983, surface science changed indelibly. Thereafter it was possible to image almost routinely surfaces and surface bound species with atomic-scale resolution. Not long afterward, Eigler and Schweizer[4] demonstrated that matter could be manipulated on an atom by atom basis. Furthermore, with the inexorable march of smaller, faster, cheaper, better in the semiconductor device industry, technology was marching closer and closer to surfaces. The STM has allowed us to visualize quantum mechanics as never before. As an example, we show two images of a Si(100) surface. In one case, Figure I.1(a), a bonding state is imaged. In the other, Figure I.1(b) an antibonding state is shown. Just as expected, the antibonding state exhibits a node between the atoms whereas the bonding state exhibits enhanced electron density between the atoms.

Surface science had always been about nanoscale science, even though it was never phrased that way. Catalysis has been the traditional realm of surface chemistry. With the advent of nanotechnology, it became apparent that the control of matter on the molecular scale at surfaces was of much wider relevance. This book is an attempt, from the point of view of a dynamicist, to approach surface science as the underpinning science of both heterogeneous catalysis and nanotechnology.

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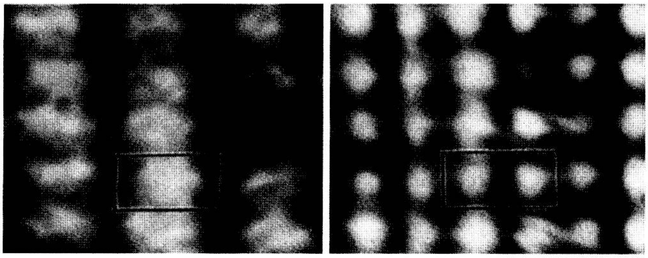


Figure I.1 *Bonding and antibonding electronic states on the Si(100) surface as imaged by STM. Reproduced from R.J. Hamers P. et al. Phys. Rev. Lett.,* **59***, 2071. ©1987 with permission of the American Physical Society.*

I.1 Heterogeneous Catalysis

One of the great motivations for studying chemical reactions on surfaces is the will to understand heterogeneous catalytic reactions. Heterogeneous catalysis is the basis of the chemical industry. *Heterogeneous* catalysis is involved in literally billions of pounds' worth of economic activity. Neither the chemical industry nor civilization would exist, as we know them today, if it were not for the successful implementation of heterogeneous catalysis. At the beginning of the 20th century, the human condition was fundamentally changed by the transformation of nitrogen on nanoscale, potassium promoted, iron catalysts to ammonia and ultimately fertilizer. Undoubtedly, catalysts are the most successful implementation of nanotechnology, not only contributing towards roughly one third of the material GDP of the US economy[5], but also supporting an additional 3.2 billion people beyond what the Earth could otherwise sustain[6]. One aim of this book is to understand why catalytic activity occurs and how we can control it.

First we should define what we mean by catalysis and a *catalyst.* The term catalysis (from the Greek *λυσιζ* and *κατα*, roughly 'wholly loosening') was coined by *Berzelius* in 1836[7]. Armstrong proposed the word catalyst in 1885. A catalyst is an active chemical spectator. It takes part in a reaction but is not consumed. A catalyst produces its effect by changing activation barriers as shown in Figure I.2. As noted by *Ostwald*, the primary contribution for which he received the Nobel Prize in chemistry in 1909, a catalyst speeds up a reaction; however, it does not change the properties of the equilibrated state. It does so by lowering the height of an activation barrier. Remember that whereas the kinetics of a reaction is determined by the relative heights of activation barriers (in combination with Arrhenius pre-exponential factors), the equilibrium constants are determined by the relative energetic positions of the initial and final states.

Nonetheless, the acceleration of reactions is not the only key factor in catalytic activity. If catalysts only accelerated reactions, they would not be nearly as important or as effective as they actually are. Catalysts can be designed not only to accelerate reactions: the best of them can also perform this task *selectively*. In other words, it is important for catalysts to speed up the right reactions, not simply every reaction. This

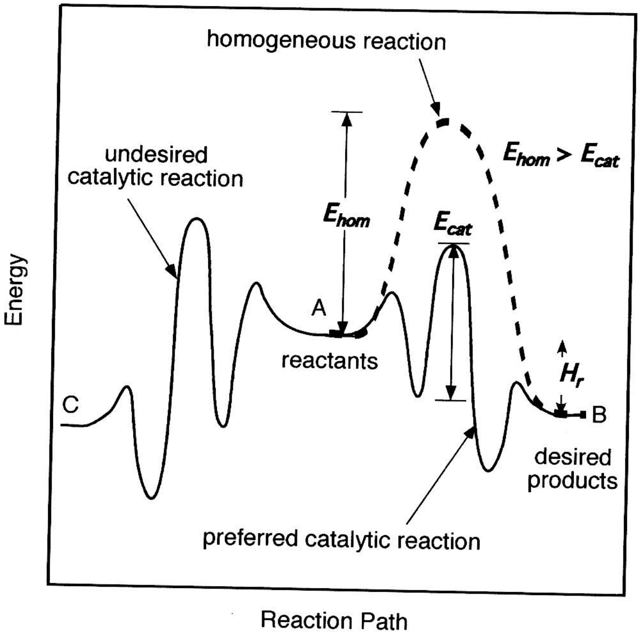


Figure I.2 *Activation energies and their relationship to an active and selective catalyst. A, reactants; B, desired product; C undesired product; E_{hom}, activation barrier for the homogeneous reaction; E_{cat}, activation barrier with use of a catalyst; $\Delta_r H$, change in enthalpy of reactants compared with products.*

is also illustrated in Figure I.2 wherein the activation barrier for the desired product B is decreased more than the barrier for the undesired product C.

I.2 Why Surfaces?

Heterogeneous reactions occur in systems in which two or more phases are present, for instance, solids and liquids or gases and solids. The reactions occur at the interface between these phases. The interfaces are where the two phases meet. Liquid/solid and gas/solid interfaces are of particular interest because the surface of a solid gives us a place to deposit and immobilize a catalytic substance. By immobilizing the catalyst, we can ensure that it is not washed away and lost in the stream of products that are made. Very often catalysts take the form of small particles (the active agent) attached to the surfaces of high surface area solids (the substrate).

However, surfaces are of particular interest not only because they are where phases meet and because they give us a place to put catalysts. The surface of a solid is inherently different from the rest of the solid (the bulk). The bonding at the surface is different from in the bulk; therefore, we should expect the chemistry of the surface to be unique. Surface atoms simply cannot satisfy their bonding requirements in the same way as bulk atoms.

Therefore, surface atoms will always want to react in some way, either with each other or with foreign atoms, to satisfy their bonding requirements.

I.3 Where are Heterogeneous Reactions Important?

To illustrate a variety of topics in heterogeneous catalysis, I will make reference to a list of catalytic reaction systems that I label the (unofficial) Industrial Chemistry Hall of Fame. These reactions are selected not only because they demonstrate a variety of important chemical concepts, but also because they have also been of particular importance both historically and politically.

I.3.1 Haber-Bosch Process

$$N_2 + 3H_2 \rightarrow 2NH_3$$

Nitrogen fertilizers underpin modern agriculture. The inexpensive production of fertilizers would not be possible without the *Haber-Bosch process*. Ammonia synthesis is almost exclusively performed over an alkali metal promoted Fe catalyst invented by *Haber*, optimized by *Mittasch* and commercialized by *Bosch*. The establishment of the Haber-Bosch process is a fascinating story[6]. Ostwald (who misinterpreted his results), Nernst (who thought yields were intolerably low and abandoned further work), and Le Châtelier (who abandoned his work after an explosion in his laboratory), all could have discovered the secret of ammonia synthesis but did not. Technical innovations such as lower pressure reforming and synthesis, better catalysts and integrated process designs have reduced the energy consumption per ton of fixed nitrogen from 120 GJ to roughly 30 GJ, which is only slightly above the thermodynamic limit. This represents an enormous cost and energy usage reduction since over 120 million metric tons (MMt) of NH_3 are produced each year.

Ammonia synthesis is a structure sensitive reaction. Already a number of questions arise. Why an Fe catalyst? Why is the reaction run at high pressure and temperature? What do we mean by promoted and why does an alkali metal act as a promoter? What is a structure sensitive reaction? What is the reforming reaction used to produce hydrogen and how is it catalysed? By the end of this book all of the answers should be clear.

I.3.2 Fischer-Tropsch Chemistry

$$H_2 + CO \rightarrow \text{methanol or liquid fuels or other hydrocarbons (HC) and oxygenates}$$

Fischer-Tropsch chemistry transforms synthesis gas ($H_2 + CO$, also called syngas) into useful fuels and intermediate chemicals. It is the basis of the synthetic fuels industry and has been important in sustaining economies that were shut off from crude oil, two examples of which were Germany in the 1930s and 1940s and more recently South Africa. It represents a method of transforming either natural gas or coal into more useful chemical intermediates and fuels. Interest in Fischer-Tropsch chemistry is rising again because in addition to these feedstocks, biomass may also be used to produce synthesis gas, which is then converted to diesel or synthetic crude oil.

Fischer-Tropsch reactions are often carried out over Fe or Co catalysts. However while Fischer-Tropsch is a darling of research laboratories, industrialists often shy away from it because selectivity is a major concern. A nonselective process is a costly one and numerous products are possible in FT synthesis while only a select few are desired for any particular application.

I.3.3 Three-way Catalyst

$$\mathrm{NO}_x,\ \mathrm{CO\ and\ HC} \rightarrow \mathrm{H_2O} + \mathrm{CO_2} + \mathrm{N_2}$$

Catalysis is not always about creating the right molecule. It can equally well be important to destroy the right molecules. Increasing automobile use translates into increasing necessity to reduce automotive pollution. The catalytic conversion of noxious exhaust gases to more benign chemicals has made a massive contribution to the reduction of automotive pollution. The three-way catalyst is composed of Pt, Rh and Pd. Pb rapidly poisons the catalyst. How does this poisoning (loss of reactivity) occur?

I.4 Semiconductor Processing and Nanotechnology

The above is the traditional realm of heterogeneous catalytic chemistry. However, modern surface science is composed of other areas as well and has become particularly important to the world of micro- and *nanotechnology*[8]. The latest microprocessors now incorporate critical dimensions of only 45 nm in width and this will soon drop to 32 nm. The thickness of insulating oxide layers is now only 4–5 atomic layers. Obviously, there is a need to understand materials properties and chemical reactivity at the molecular level if semiconductor processing is to continue to advance to even smaller dimensions. It has already been established that surface cleanliness is one of the major factors affecting device reliability. Eventually, however, the engineers will run out of 'room at the bottom'. Furthermore, as length scales shrink, the effects of quantum mechanics inevitably become of paramount importance. This has led to the thought that a whole new device world may exist, which is ruled by quantum mechanical effects. Devices such as a single electron transistor have been built. Continued fabrication and study of such devices requires an understanding of atomic Legos – the construction of structures on an atom-by-atom basis.

Figure I.3 shows images of some devices and structures that have been crafted at surfaces. Not only electronic devices are of interest. Microelectromechanical and nanoelectromechanical systems (MEMS and NEMS) are attracting increasing interest. The first commercial example is the accelerometer that triggers airbags in cars. These structures are made by a series of surface etching and growth reactions.

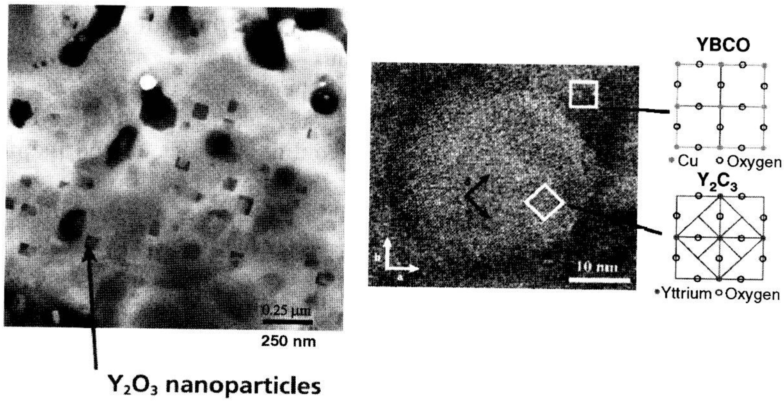
The ultimate control of growth and etching would be to perform these one atom at a time. Figure I.4 demonstrates how H atoms can be removed one by one from a Si surface. The uncovered atoms are subsequently covered with oxygen and then etched. In Figure I.4(b) we see a structure built out of Xe atoms. There are numerous ways to create structures at surfaces. We will investigate several of these in which the architect must actively pattern the substrate. We will also investigate self-assembled structures, that is, structures that form spontaneously without the need to push around the atoms or molecules that compose the structure.

I.5 Other Areas of Relevance

Surface science touches on a vast array of applications and basic science. The fields of corrosion, adhesion and tribology are all closely related to interfacial properties. The importance of heterogeneous processes in atmospheric and interstellar chemistry has now been realized. Virtually all of the molecular hydrogen that exists in the interstellar medium had to be formed on the surfaces of grains and dust particles. The role of surface chemistry in the formation of the over 100 other molecules that have been detected in outer space remains an open question.[9,10] Many electrochemical reactions occur heterogeneously. Our understanding of charge transfer at interfaces and the effects of surface structure and adsorbed species remain in a rudimentary state.

I.6 Structure of the Book

The aim of this book is to provide an understanding of chemical transformations and the formation of structures at surfaces. To do these we need (1) to assemble the appropriate vocabulary and (2) to gain a familiarity with an arsenal of tools and a set of principles



(a)

(b)

Figure I.3 *Examples of devices and structures that are made by means of surface reactions, etching and growth. (a) Transmission electron micrograph of yttria (Y_2O_3) nanocrystals in an yttrium barium copper oxide (YBCO) matrix. (b) Yttria nanocrystal embedded in YBCO layer of a second generation high temperature (high T_C) superconductor. Panels (a) and (b) reproduced from M.W. Rupich et al. IEEE Transactions on Applied Superconductivity* **15**, *2611. Copyright (2002), with permission from IEEE. (c) An advanced CMOS device incorporating a low dielectric constant (low k) insulating layer. Reproduced from Ikeda et al. Proceedings of the IEEE International Interconnect Technical Conference, p. 42, from Micromachined thermoelectric generator fabricated on a silicon rim. Copyright (2006) with permission from IEEE.*