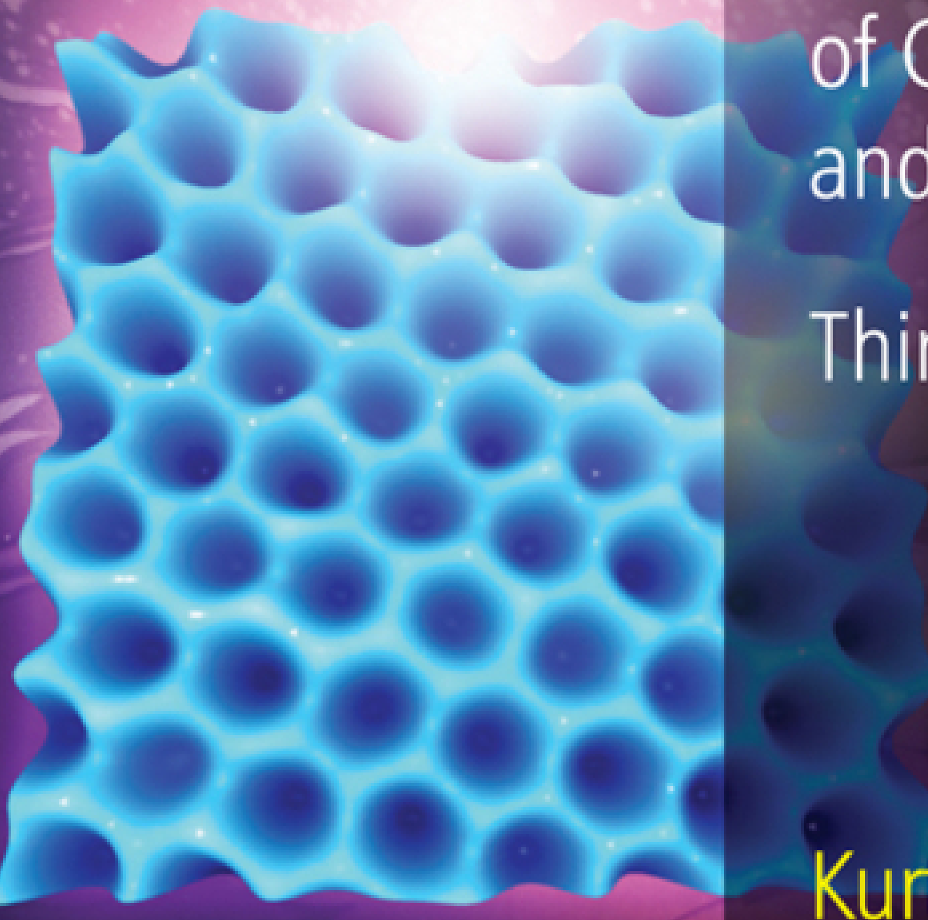


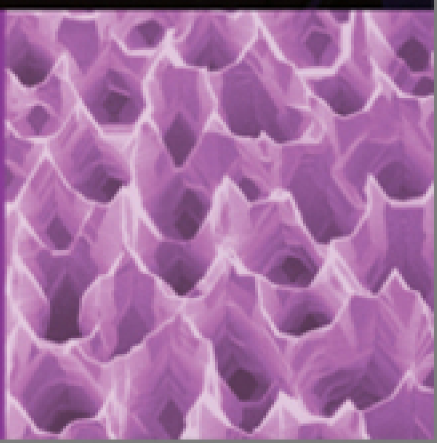
SURFACE SCIENCE

Foundations of Catalysis and Nanoscience

Third Edition

Kurt W. Kolasinski

WILEY



Surface Science

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Foundations of Catalysis and Nanoscience

Third Edition

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

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To Kirsti and Annika

Contents

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Kurt W. Kolasinski
West Chester

October 2011

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 is a good starting point for surface chemistry. But since the early 1980s, the field of surface science has changed dramatically. Binnig and Rohrer [2, 3] discovered the scanning tunnelling microscope (STM) in 1983 [3]. By 1986, they had been awarded the Nobel Prize in Physics and surface science was 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. The tremendous infrastructure of instrumentation, ideas and understanding that has been amassed in surface science is evident in the translation of the 2004 discovery of Novoselov and Geim [5] of graphene into a body of influential work recognized by the 2010 Nobel Prize in Physics.

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, two images of a Si(100) surface are shown in Fig. I.1. In one case, Fig. I.1(a), a bonding state is imaged. In the other, Fig. 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.

The STM ushered in the age of nanoscience; however, surface science has always been about nanoscience, even when it was not phrased that way. Catalysis has been the traditional realm of surface chemistry, and 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". While it was Irving Langmuir's work – Nobel Prize in Chemistry, 1932 – 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.

Of course, these are not the only scientists to have contributed to the growth of understanding in surface science, nor even the only Nobel Prize winners. In the pages that follow, you will be introduced to many more scientists and, hopefully, to many more insights developed by all of them. 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.

Surface Science: Foundations of Catalysis and Nanoscience, Third Edition. Kurt W. Kolasinski.

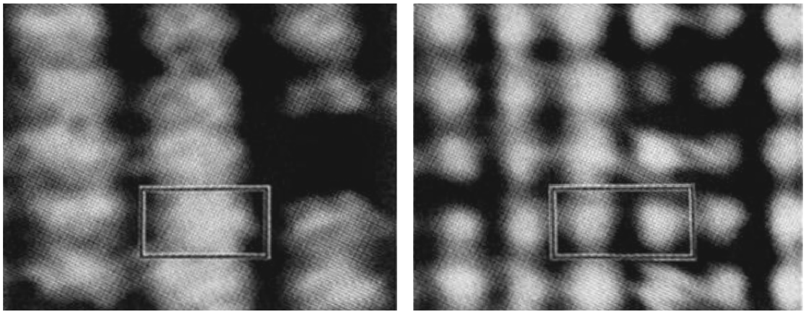


Figure I.1 Bonding and antibonding electronic states on the Si(100) surface as imaged by STM. Reproduced with permission from R.J. Hamers, P. Avouris and F. Bozso, Phys. Rev. Lett. *59 (1987) 2071. ©1987 by the American Physical Society.*

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 dollars 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,

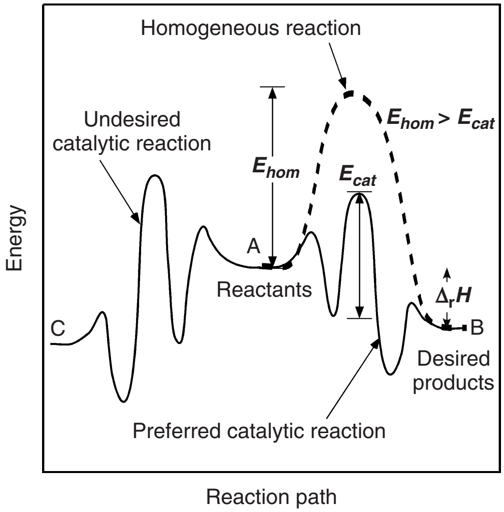


Figure I.2 Activation energies and their relationship to an active and selective catalyst, which transforms A, the reactant, into B, the desired product, rather than C, the undesired product. E_{hom}, activation barrier for the homogeneous reaction; E_{cat}, activation barrier with use of a catalyst;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

not only contributing towards roughly 1/3 of the material GDP of the US economy [6], but also supporting an additional 3.2 billion people beyond what the Earth could otherwise sustain [7]. 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 $\lambda\nu\sigma\iota\zeta$ and $\kappa\alpha\tau\alpha$, roughly "wholly loosening") was coined by Berzelius in 1836 [8]. 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 Fig. I.2. As noted by Ostwald , who was awarded the Nobel Prize in Chemistry in 1909 primarily for this contribution, 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 constant is determined by the Gibbs energy of the initial state relative to the final state.

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 is also illustrated in Fig. 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 and reactants meet, where charge exchange occurs. 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 nanoparticles (the active agent) attached to the surfaces of high surface area porous 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 than the rest of the solid (the bulk) because its bonding is different. 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 have a propensity 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 reactions 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 [7]. 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 [7]. 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 lab), 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 130 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 catalyzed? 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 chemistry, at least in part, that makes synthetic oils that last 8000 km instead of 5000 km. 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, not only because of the discovery of new and improved capture from old sources of natural gas, but also because biomass may also be used to produce synthesis gas, which is then converted to diesel or synthetic crude oil [9].

Fischer-Tropsch reactions are often carried out over Fe or Co catalysts. However, while Fischer-Tropsch is a darling of research labs, 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

$$NO_x, CO \text{ and } HC \rightarrow H_2O + CO_2 + N_2$$

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 gasses 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 [10–12]. Critical dimensions in microprocessors dropped below 100 nm in 2004 and now stand at 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, which triggers airbags in cars and lets your iPhone™ know whether it should present its display in landscape or portrait mode. 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, then etched. In Fig. 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 been realized [13]. 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 active area of research [14–16]. 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 but improving state [17–21].

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 to (i) assemble the appropriate vocabulary, and (ii) gain a familiarity with an arsenal of tools and a set of principles that guide our thinking, aid interpretation and enhance prediction. Chapter 1 introduces us to the structure (geometric, electronic and vibrational) of surfaces and adsorbates. This gives us a picture of what surfaces look like, and how they compare to molecules and bulk materials. Chapter 2 introduces the techniques with which we look at surfaces. We quickly learn that surfaces present some unique experimental difficulties. This chapter might be skipped in a first introduction to surface science. However, some of the techniques are themselves methods for surface modification. In addition, a deeper insight into surface processes is gained by understanding the manner in which data are obtained. Finally, a proper reading of the literature cannot be made without an appreciation of the capabilities and limitations of the experimental techniques.

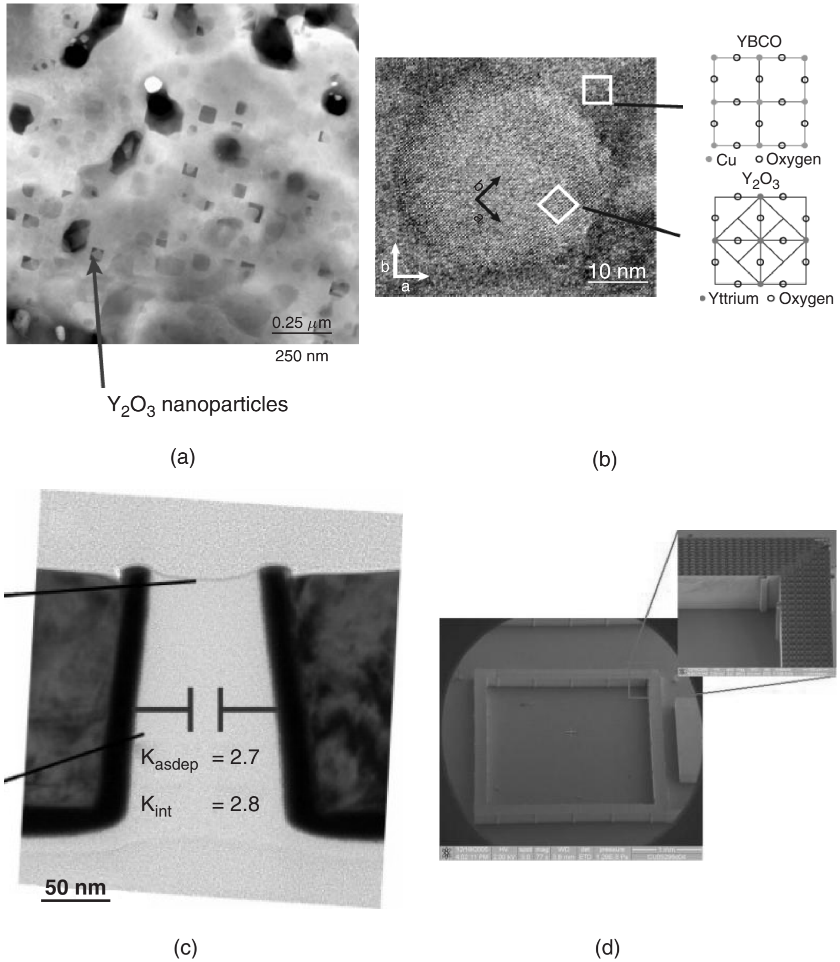
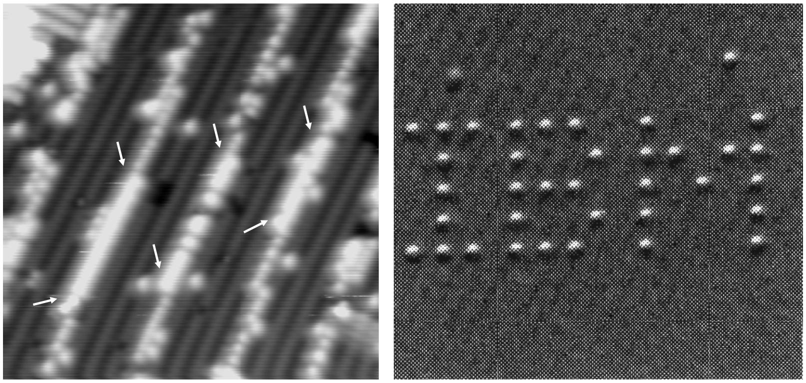


Figure I.3 *Examples of devices and structures that are made by means of surface reactions, etching and growth. (a) Transmission electron micrograph of yttria (Y_2O_3) nanocrystals in an yttrium barium copper oxide (YBCO) matrix. (b) Yttria nanocrystal embedded in YBCO layer of a second generation high temperature (high T_c) superconductor. Panels (a) and (b) reproduced from M. W. Rupich et al.,* IEEE Transactions on Applied Superconductivity *15, 2611. Copyright (2003), with permission from the IEEE. (c) An advanced CMOS device incorporating a low dielectric constant (low k) insulating layer. Reproduced from T. Torfs, V. Leonov, R. J. M. Vullers,* Sensors and Transducers Journal*, 80, 1230. Copyright (2007), with permission from the International Frequency Sensor Association (http://www.sensorsportal.com). (d) Micromachined thermoelectric generator fabricated on a silicon rim.*

After these foundations have been set in the first two chapters, the next two chapters elucidate dynamical, thermodynamic and kinetic principles concentrating on the gas/solid interface. These principles allow us to understand how and why chemical transformations occur at surfaces. They deliver the mental tools required to interpret the data encountered at liquid interfaces (Chapter 5) as well as in catalysis (Chapter 6), and growth and etching (Chapter 7) studies. Finally, in Chapter 8, we end with a chapter that resides squarely



(a) (b)

Figure I.4 *Examples of surface manipulation with atomic-scale resolution. (a) Nanolithography can be performed on a hydrogen-terminated silicon surface using a scanning tunnelling microscope (STM) tip to remove H atoms one at a time from the surface. (b) Individual Xe atoms can be moved with precision by an STM tip to write on surfaces. Panel (a) reproduced with permission from T.-C. Shen, C. Wang, G. C. Abeln, J. R. Tucker, J. W. Lyding, P. Avouris and R. E. Walkup,* Science *268 (1995) 1590. © 1995 American Association for the Advancement of Science. Panel (b) reproduced with permission from D. M. Eigler and E. K. Schweizer,* Nature *344 (2000) 524. © 2000 Macmillan Magazines Ltd.*

at the frontier of our knowledge: an investigation of the interfacial process probed and exited by photons, electrons and proximal probes.

Each chapter builds from simple principles to more advanced ones. Each chapter is sprinkled with Advanced Topics. The Advanced Topics serve two purposes. First, they provide material beyond the introductory level and can be skipped so as not to interrupt the flow of the introductory material. Second, they highlight some frontier areas. The frontiers are often too complex to explain in depth at the introductory level; nonetheless, they are included to provide a taste of the exciting possibilities of what can be done with surface science. Each chapter is also accompanied by exercises. The exercises act not only to demonstrate concepts arising in the text, but also as extensions to the text. They truly are an integral part of the whole and their solutions comprise the last eight chapters of this book. The exercises are not meant to be mere problems with answers to look up. Rather, they are intended to be exercises in problem solving applying the material in the text. The solutions, therefore, not only highlight and extend the material covered in the first eight chapters, they also detail methods of problem solving and the melding of concepts with mathematics to develop answers. Additional exercises can be found at the website that supports this book http://courses.wcupa.edu/kkolasinski/surfacescience/.

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Energy

1 eV	1.602176×10^{-19} J
1 eV/*hc*	8065.5 cm^{-1}
1 meV/*hc*	8.0655 cm^{-1}
1 eV/particle	96.485 kJ mol^{-1}
1 kcal mol^{-1}	4.184 kJ mol^{-1}

Impingement Rate

$Z_\mathrm{w} = N_\mathrm{A} p (2\pi MRT)^{-1/2}$	M = molar mass
$Z_\mathrm{w} = p(2\pi m k_\mathrm{B} T)^{-1/2}$	m = particle mass
$Z_\mathrm{w} = 3.51 \times 10^{22}\ \mathrm{cm}^{-2}\ \mathrm{s}^{-1}(p/\sqrt{MT})$	Z_w in $\mathrm{cm}^{-2}\ \mathrm{s}^{-1}$, M in g mol^{-1}, p in torr, T in K
$Z_\mathrm{w} = 2.63 \times 10^{24}\ \mathrm{m}^{-2}\ \mathrm{s}^{-1}(p/\sqrt{MT})$	Z_w in $\mathrm{m}^{-2}\ \mathrm{s}^{-1}$, M in g mol^{-1}, p in Pa

Pressure

1 atm =	101325 Pa = 1013.25 mbar = 760 torr
1 bar =	10^5 Pa
1 torr =	1.3332 mbar = 133.32 Pa

Quantity	**Symbol**	**Value**		**Units**
Boltzmann constant	k_B	1.38066	10^{-23}	J K^{-1}
		8.61741	10^{-5}	eV K^{-1}
Planck constant	h	6.62608	10^{-34}	J s
	$\hbar = h/2\pi$	1.05457	10^{-34}	J s
Avogadro constant	N_A	6.02214	10^{23}	mol^{-1}
Bohr radius	a_0	5.29177	10^{-11}	m
Rydberg constant	R_∞	1.09737	10^{5}	cm^{-1}
Speed of light	c	2.99792458	10^{8}	m s^{-1}
Faraday constant	$F = N_\mathrm{A} e$	9.64853	10^{4}	C mol^{-1}
Elementary charge	e	1.602176	10^{-19}	C
Gas constant	$R = N_\mathrm{A} k_\mathrm{B}$	8.31451		J K^{-1} mol^{-1}
Vacuum permittivity	ε_0	8.85419	10^{-12}	J^{-1} C^{2} m^{-1}
Atomic mass unit	u	1.66054	10^{-27}	kg
Electron mass	m_e	9.10939	10^{-31}	kg
Proton mass	m_p	1.67262	10^{-27}	kg
Neutron mass	m_n	1.67493	10^{-27}	kg

1

Surface and Adsorbate Structure

We begin with some order of magnitude estimates and rules of thumb that will be justified in the remainder of this book. These estimates and rules introduce and underpin many of the most important concepts in surface science. The atom density in a solid surface is roughly 10^{15} cm^{-2} (10^{19} m^{-2}). The Hertz-Knudsen equation

$$Z_w = \frac{p}{(2\pi m k_B T)^{1/2}} \tag{1.0.1}$$

relates the flux of molecules striking a surface, Z_w, to the pressure (or, equivalently, the number density). Combining these two, we find that if the probability that a molecule stays on the surface after it strikes it (known as the sticking coefficient s) is unity, then it takes roughly 1 s for a surface to become covered with a film one molecule thick (a monolayer) when the pressure is 1×10^{-6} Torr. The process of molecules sticking to a surface is called adsorption. If we heat up the surface with a linear temperature ramp, the molecules will eventually leave the surface (desorb) in a well-defined thermal desorption peak, and the rate of desorption at the top of this peak is roughly one monolayer per second. When molecules adsorb via chemical interactions, they tend to stick to well-defined sites on the surface. An essential difference between surface kinetics and kinetics in other phases is that we need to keep track of the number of empty sites. Creating new surface area is energetically costly and creates a region that is different from the bulk material. Size dependent effects lie at the root of nanoscience, and two of the primary causes of size dependence are quantum confinement and the overwhelming of bulk properties by the contributions from surfaces.

We need to understand the structure of clean and adsorbate-covered surfaces and use this as a foundation for understanding surface chemical processes. We will use our knowledge of surface structure to develop a new strand of chemical intuition that will allow us to know when we can apply things that we have learned from reaction dynamics in other phases and when we need to develop something completely different to understand reactivity in the adsorbed phase.

What do we mean by surface structure? There are two inseparable aspects to structure: electronic structure and geometric structure. The two aspects of structure are inherently coupled and we should never forget this point. Nonetheless, it is pedagogically helpful to separate these two aspects when we attack them experimentally and in the ways that we conceive of them.

When we speak of structure in surface science we can further subdivide the discussion into that of the clean surface, the surface in the presence of an adsorbate (substrate structure) and that of the adsorbate

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(adsorbate structure or overlayer structure). That is, we frequently refer to the structure of the first few layers of the substrate with and without an adsorbed layer on top of it. We can in addition speak of the structure of the adsorbed layer itself. Adsorbate structure not only refers to how the adsorbed molecules are bound with respect to the substrate atoms but also how they are bound with respect to one another.

1.1 Clean surface structure

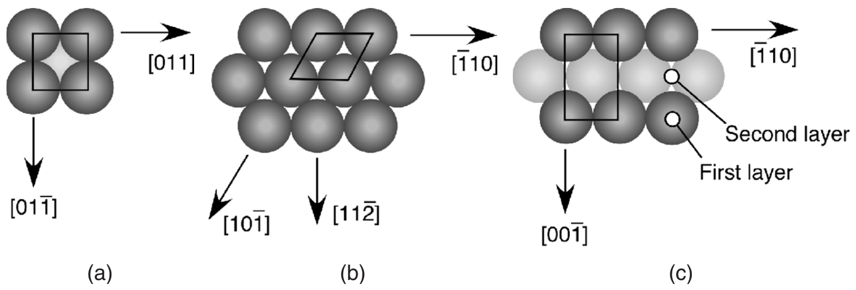
1.1.1 Ideal flat surfaces

Most of the discussion here centres on transition metal and semiconductor surfaces. First we consider the type of surface we obtain by truncating the bulk structure of a perfect crystal. The most important crystallographic structures of metals are the face-centred cubic (fcc), body-centred cubic (bcc) and hexagonal close-packed (hcp) structures. Many transition metals of interest in catalysis take up fcc structures under normal conditions. Notable exceptions are Fe, Mo and W, which assume bcc structures and Co and Ru, which assume hcp structures. The most important structure for elemental (group IV: C, Si, Ge) semiconductors is the diamond lattice whereas compound semiconductors from groups III and V (III-V compounds, e.g. GaAs and InP) assume the related zincblende structure.

A perfect crystal can be cut along any arbitrary angle. The directions in a lattice are indicated by the Miller indices. Miller indices are related to the positions of the atoms in the lattice. Directions are uniquely defined by a set of three (fcc, bcc and diamond) or four (hcp) rational numbers and are denoted by enclosing these numbers in square brackets, e.g. [100]. hcp surfaces can also be defined by three unique indices and both notations are encountered as shown in Fig. 1.3. A plane of atoms is uniquely defined by the direction that is normal to the plane. To distinguish a plane from a direction, a plane is denoted by enclosing the numbers associated with the defining direction in parentheses, e.g. (100). The set of all related planes with permutations of indices, e.g. (100), (010), (001) etc, is denoted by curly brackets such as {001}.

The most important planes to learn by heart are the low index planes. Low index planes can be thought of as the basic building blocks of surface structure as they represent some of the simplest and flattest of the fundamental planes. The low-index planes in the fcc system, e.g. (100), (110) and (111), are shown in Fig. 1.1. The low-index planes of bcc symmetry are displayed in Fig. 1.2, and the more complex structures of the hcp symmetry are shown in Fig. 1.3.

The ideal structures shown in Fig. 1.1 demonstrate several interesting properties. Note that these surfaces are not perfectly isotropic. We can pick out several high-symmetry sites on any of these surfaces that are geometrically unique. On the (100) surface we can identify sites of one-fold (on top of and at the centre of



(a) (b) (c)

Figure 1.1 *Hard sphere representations of face-centred cubic (fcc) low index planes: (a) fcc(100); (b) fcc(111); (c) fcc(110).*

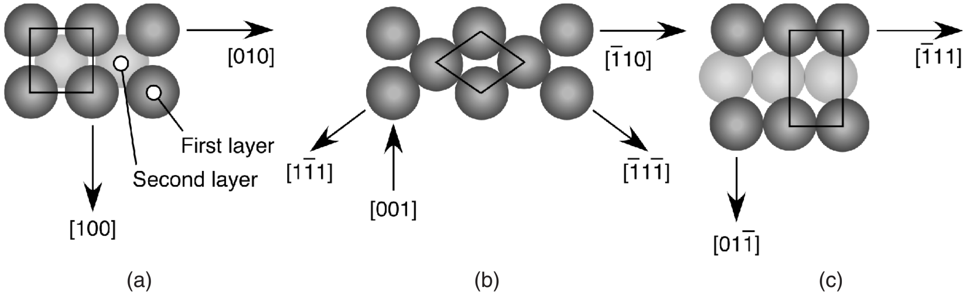


Figure 1.2 *Hard sphere representations of body-centred cubic (bcc) low index planes: (a) bcc(100); (b) bcc(110); (c) bcc(211).*

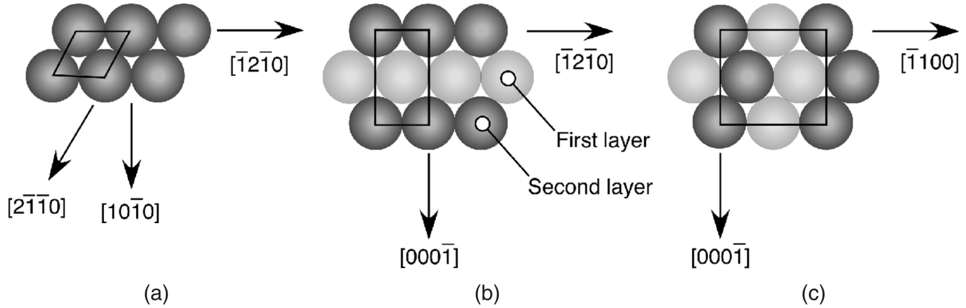


Figure 1.3 *Hard_sphere representations of_hexagonal close-packed (hcp) low index planes: (a) hcp*(001) = (0001)*; (b) hcp*$(10\bar{1}0)$ = *hcp*(100)*; (c) hcp*$(11\bar{2}0)$ = *hcp*(110)*.*

one atom), two-fold (bridging two atoms) or four-fold co-ordination (in the hollow between four atoms). The co-ordination number is equal to the number of surface atoms bound directly to the adsorbate. The (111) surface has one-fold, two-fold and three-fold co-ordinated sites. Among others, the (110) presents two different types of two-fold sites: a long bridge site between two atoms on adjacent rows and a short bridge site between two atoms in the same row. As one might expect based on the results of co-ordination chemistry, the multitude of sites on these surfaces leads to heterogeneity in the interactions of molecules with the surfaces. This is important in our discussions of adsorbate structure and surface chemistry.

A very useful number is the surface atom density, σ_0. Nicholas [1] has shown that there is a simple relationship between σ_0 and the Miller indices *hkl*,

$$\sigma_0 = \frac{1}{A_{hkl}} = \frac{4}{Qa^2(h^2 + k^2 + l^2)^{1/2}} \quad \text{for fcc and bcc} \tag{1.1.1}$$

and

$$\sigma_0 = \frac{1}{A_{hkl}} = \frac{2}{a^2[4r^2(h^2 + hk + k^2) + 3l^2]^{1/2}} \quad \text{for hcp} \tag{1.1.2}$$