REACTIONS AT SOLID SURFACES

GERHARD ERTL
Fritz-Haber-Institut der
Max-Planck-Gesellschaft
Berlin, Germany

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PREFACE

Professors H. Abruña and M. Hines kindly invited me to deliver the 2007 Baker Lectures at the Department of Chemistry and Chemical Biology of Cornell University. Hence, in the spring that year, my wife and I spent a few weeks in Ithaca, New York, where I presented a series of lectures to people of different scientific backgrounds. We are very grateful to our hosts and all members of the department who made this stay so pleasant and inspiring. When I was asked afterward to write a book based upon the lectures for John Wiley & Sons, it was a pleasure for me to accept this request. The text herewith closely follows the eight lectures that were delivered at the 2007 Baker Lecture Series, and the content presented is essentially based on results obtained in the author's own laboratory. That is why it is not a comprehensive review, but rather a subjective picture of the field covered, reactions at solid surfaces. I have to, therefore, apologize for the fact that important work by other researchers will be inadequately represented.

I am very much indebted to my numerous coworkers who collaborated with me over many years. In addition, I am very grateful to Waruno Mahdi for careful preparation of the figures and to Marion Reimers for typing the text.

GERHARD ERTL
Berlin, November 2008

CHAPTER

1

BASIC PRINCIPLES

1.1. INTRODUCTION: THE SURFACE SCIENCE APPROACH

A solid body is always terminated by surfaces where the atoms have a different environment (e.g., fewer nearest neighbors) from that in the bulk. As a consequence, these surface atoms will exhibit altered chemical reactivity. Unsaturated valencies will give rise to bond formation with particles impinging from the adjacent (gaseous or liquid) phase, and these "chemisorbed" species will in turn differ in reactivity from that in the absence of the surface. This is the basic principle underlying the phenomenon of heterogeneous catalysis. Deposition of material beyond the first monolayer leads to nucleation of a new phase and eventually to crystal growth (epitaxy). Control of these processes on the nanometer scale is of crucial importance, for example, for semiconductor microtechnology, and the whole field of "nanotechnology" is in fact essentially governed by surface reactions. Atoms can, on the other hand, also be removed from the surface, either thermally or, if this process is associated with charge transfer across the interface,

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with the aid of a proper electric potential. These electrochemical reactions are underlying the processes of etching or corrosion.

This text is intended to outline our present understanding of the fundamental processes underlying reactions at solid surfaces instead of attempting to provide a full overview. For this reason, the discussion will essentially be restricted to the simplest situations: processes occurring only in two dimensions, that is, involving chemisorbed phases, on surfaces consisting of only one element, that is, metals. This scenario is found with a large variety of heterogeneously catalyzed reactions for which a few case studies will be discussed later.

Since the rate of such a reaction is proportional to the area of the exposed surface, catalysts generally exhibit a high specific surface area. Apart from the use of highly porous materials with large "internal" surface areas (e.g., zeolites), this is mostly achieved by depositing small particles of the active catalyst material onto (more or less) inert high surface area supports. Figure 1.1 shows a high-resolution electron micrograph of a Ru catalyst on a MgO support together with a cartoon illustrating the different crystal planes and edge atoms acting as active sites [1]. The catalyst particles have indeed diameters of only a few nanometers or even less: In fact, heterogeneous catalysis has been a nanotechnology for more than a hundred years, long before this term was introduced. Metal particles consisting only of a very small number of atoms may exhibit electronic properties and hence chemical reactivity different from those of the bulk material. A prominent example for this effect is offered by gold: While the bulk material is catalytically practically inert, very small particles or thin films may exhibit extraordinary activities [2], and this is a field of great current interest. However, alterations of the bulk electronic properties of the catalyst particles will be ignored in the following.

But there is another effect that may have utmost influence on the reactivity: Small catalyst particles exhibit different crystal planes together with structural defects and chemisorbed foreign

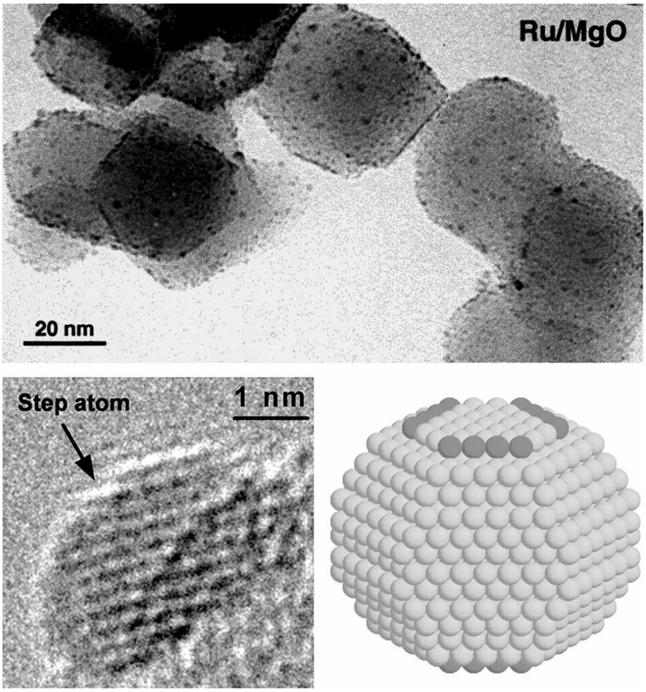


FIGURE 1.1. High-resolution electron micrograph from a small Ru particle on a MgO support together with a sketch of its structure [1].

atoms. All these effects render the surface chemistry of a "real" catalyst rather complex. A solution to this problem was already proposed by Langmuir [3] in 1922:

> Most finely divided catalysts must have structures of great complexity. In order to simplify our theoretical consideration of reactions at surfaces, let us confine our attention to plane surfaces. If the principles in this case are well understood, it should then be possible to extend the theory to the case of porous bodies. In general, we should look upon the surface as consisting of a checkerboard . . .

What Langmuir had in mind were clean, well-defined single-crystal surfaces that can now be prepared and investigated through the introduction of ultrahigh vacuum techniques and the development of a whole arsenal of surface physical methods.

Since the latter in most cases cannot be operated at the high-pressure conditions of "real" catalysis, this causes the appearance of a "pressure gap." And since the properties of well-defined single-crystal surfaces will generally be quite different from the surface properties of "real" catalysts, this gives rise to the so-called "materials gap." That these gaps can indeed be overcome will be demonstrated by some of the examples to be presented.

One of the leading researchers of "classical" catalysis expressed his opinion about this "surface science approach" as follows [4]: "Catalysis is a kinetic phenomenon. The urgent need for rate constants demands the support of surface science."

The physical tools for chemical analysis of surfaces as well as for investigation of their structural, electronic, vibrational, and dynamic properties have been described quite extensively in the literature [5–11], so we refrain here from repetitions. Scanning probe techniques, and in particular the scanning tunneling microscope [12], proved to be most powerful for direct observation of processes on atomic scale.

1.2. ENERGETICS OF CHEMISORPTION

Apart from ubiquitous van der Waals interactions leading to a weak physisorption bond, particles impinging onto a solid surface may experience chemical bond formation called chemisorption—a concept originally suggested by Haber [13] and somewhat later substantiated by Langmuir [14]. This bond formation may keep the molecular entity intact (nondissociative chemisorption), or it may be associated with bond breaking and separation of the fragments on the surface (dissociative chemisorption). The reverse processes are called desorption. The strength of the chemisorption bond (i.e., chemisorption energy) may be directly determined by calorimetry. Recent developments even provide such data from single crystals, but these techniques are elaborate and hence applied only in a few laboratories [15,16]. If adsorption is in equilibrium with desorption, determination of the coverage Θ as a function of partial pressure p and temperature T provides E_{ad} through application of the Clausius–Clapeyron equation

$$\left.\frac{\mathrm{d}\ln p}{\mathrm{d}(1/T)}\right|_{\Theta=\text{const}} = -\frac{E_{\text{ad}}}{R}$$

This means a plot of $\ln p$ over $1/T$ at constant coverage Θ yields the isosteric heat of adsorption at the respective coverage. As an example, Fig. 1.2 shows the variation of E_{ad} for CO adsorbed on Pd(1 1 1) with Θ as determined in this way, where the coverage was monitored through the respective change in the work function [17]. The adsorption energy remains constant up to $\Theta = 0.33$ and then drops by 2 kcal/mol due to a change in the adsorption geometry as a consequence of the onset of repulsions between the adsorbed molecules. The full line in Fig. 1.2 shows the variation of the adsorption energy with coverage (i.e., mean distance between the adsorbed molecules) if the (slightly modified) interaction potential between free CO molecules is operating, which fits perfectly the experimental data at high coverages.

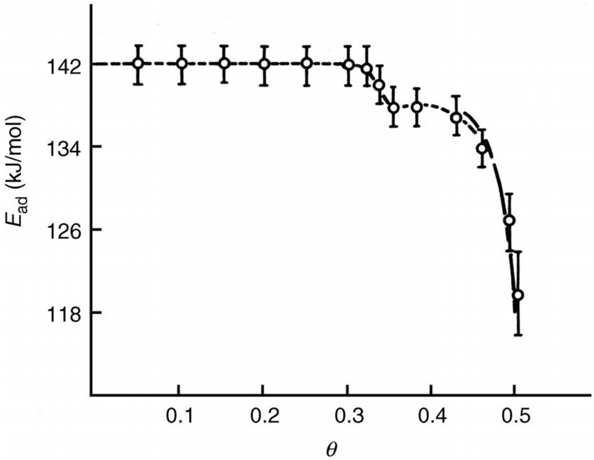


FIGURE 1.2. The adsorption energy for CO adsorbed on a Pd(1 1 1) surface as a function of coverage θ [17].

In general, interactions between adsorbates may be either repulsive or attractive. Direct repulsive interactions result from dipole–dipole interaction or from orbital overlap, but may, however, also be of indirect nature mediated through the electronic system of the substrate [29]. Attractive interactions are usually of the latter type and are analogous to the through-bond interactions in organic chemistry [18]. Figure 1.3 shows the variation of the O–O interaction potential with distance on Ru(0 0 0 1) as determined through the mean residence times of the adsorbed O atoms in different configurations [19].

The most convenient (but also least accurate) method to derive information about the adsorption energy is based on the analysis of thermal desorption spectroscopy (TDS) data [5,20]. The temperature of the adsorbate covered surface is increased continuously with a constant heating rate β (so the momentary surface

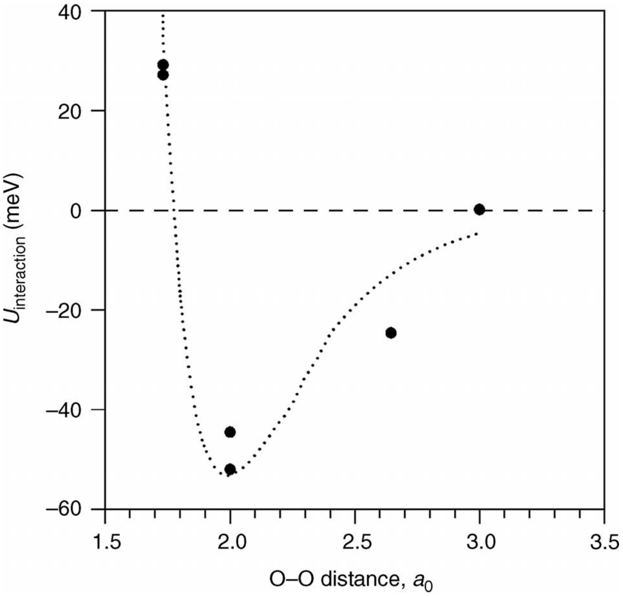


FIGURE 1.3. Variation of the interaction potential between two O atoms adsorbed on Ru(0 0 0 1) as a function of their separation (a_0 = lattice constant of the substrate surface) [19].

temperature is $T = T_0 + \beta t$), and the concentration of desorbing species is monitored by a quadrupole mass spectrometer, which at high pumping rate is proportional to the rate of desorption:

$$-\frac{\mathrm{d}n_i}{\mathrm{d}t} = \nu_i n_i^x \exp\left(-\frac{E^*_{\mathrm{ides}}}{RT}\right)$$

Here ν_i is the frequency factor ("preexponential"), x is the reaction order, and E^*_i is the activation energy for desorption. If adsorption is nonactivated, the latter quantity equals E_{ad}. The main problem lies in the fact that ν_i and x are usually unknown, so a simple determination of E_{ad} from the TDS peak temperature T_{max} [21] has to rely on reasonable assumptions of these quantities. More reliable determination has to be based on analysis of TDS peak shapes [5,22]. The preexponential ν may by regarded as representing the frequency of vibration of the adsorbed particle against the surface and is frequently assumed to be of the order of 10^{-13} s, but may actually deviate from this value by up to several orders of magnitude.

The energetics of dissociative adsorption can readily be rationalized by means of the one-dimensional potential diagram proposed by Lennard-Jones [23] and reproduced in Fig. 1.4: If a diatomic molecule A_2 approaches a surface, it will first experience (weak) bonding as $A_{2,\mathrm{ad}}$. Dissociation of the free molecule would require the dissociation energy E_{diss}, and the two atoms would then form strong bonds with the surface (A_{ad}). The crossing point of the two lines marks the activation energy for dissociative adsorption and determines the kinetics of adsorption (see below), while the adsorption energy E_{ad} for $A_2 \rightarrow 2A_{\mathrm{ad}}$ is related to the surface–adsorbate bond energy $E_{\text{S-A}}$ through $E_{\text{S-A}} = \frac{1}{2}(E_{\mathrm{ad}} + E_{\mathrm{diss}})$. In the case of noninteracting adsorbed species A_{ad}, desorption then follows second-order kinetics and the TDS traces are characterized by a shift of the peak maxima to lower temperatures with increasing coverage as can be seen from Fig. 1.5 with data from the H_2/Ni (1 0 0) system [24].

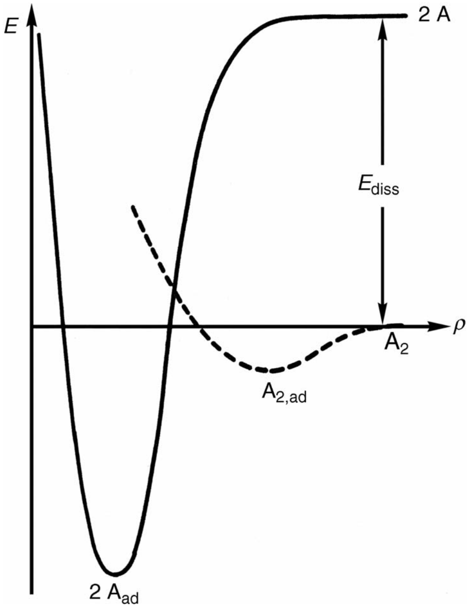

E
2 A
E_{diss}
ρ
A_2
$A_{2,\text{ad}}$
2 A_{ad}

FIGURE 1.4. Lennard-Jones diagram illustrating the energetics of dissociative adsorption.

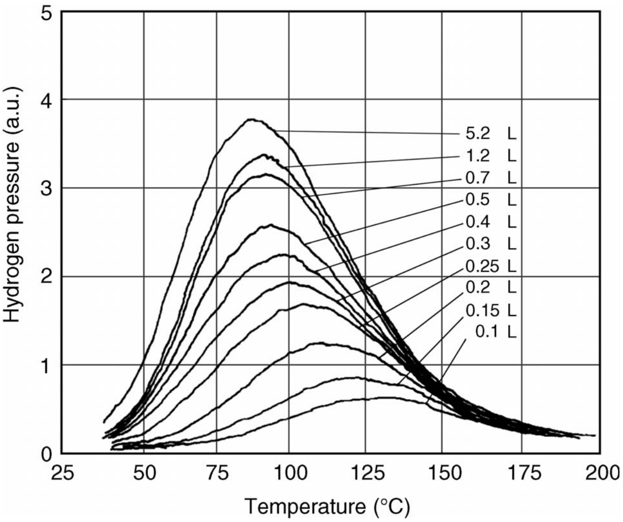


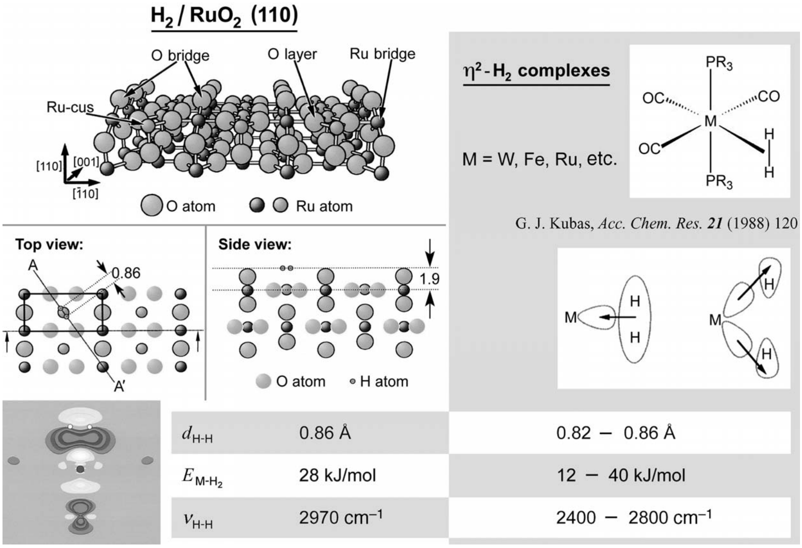
FIGURE 1.5. A series of (second-order) thermal desorption spectra for recombinative desorption of H_2 from an Ni(1 0 0) surface. Parameter is the initial exposure in Langmuir [24].

TABLE 1.1. M–CO BOND ENERGIES (KJ/MOL)

W(110)	113	Ru(0 0 0 1)	121	Ir(1 1 1)	142	Ni(1 1 1)	113
$W(CO)_6$	180	$Ru_3(CO)_{12}$	171	$Ir_4(CO)_{12}$	188	$Ni(CO)_4$	146

Chemisorption is essentially a localized phenomenon, involving mainly the adsorbate and the neighboring atoms of the adsorption site. Table 1.1 lists some data for the energy of CO chemisorption on the most densely packed planes of some transition metals together with the M–CO dissociation energies of corresponding carbonyl compounds [25]. The values for the compounds are typically larger by about 30–50%, regardless of whether mono- or multinuclear carbonyls are considered. This finding appears to be qualitatively plausible, since a surface atom is always surrounded by a larger number of neighboring atoms and therefore exhibits reduced free valency. This is confirmed by the fact that the chemisorption energy is usually higher on crystallographically more open planes. Also defects, such as monoatomic steps, are associated with higher adsorption energies, and the effect of surface structure is typically of the order of about ±10%. By moving an adsorbate across the surface, the chemisorption energy varies by a similar order of magnitude. This difference determines the activation energy for surface diffusion, which is therefore typically smaller than about 20% of the adsorption energy, so the adsorbed particle makes many jumps across the surface before it eventually desorbs.

Relations between coordination chemistry of single metal atoms and surface chemistry are illustrated by the interaction of H_2 with either a Ru atom or a $RuO_2(1\,1\,0)$ single-crystal surface [26]. As shown in Fig. 1.6, H_2 forms weakly held η^2-H_2 complexes with transition metal atoms [27], while on $RuO_2(1\,1\,0)$ the H_2 molecule is held in a similar way above the Ru atoms, where bond lengths, vibrational frequencies, and bond strengths are quite similar in both cases. However, the further reactivity is different: While with the complex compound, dissociation of the


H₂ / RuO₂ (110)
O bridge
O layer
Ru bridge
Ru-cus
[110]
[001]
[1̄10]
O atom
Ru atom
Top view:
A
0.86
A'
Side view:
1.9
O atom
H atom
η²-H₂ complexes
M = W, Fe, Ru, etc.
PR₃
OC
CO
M
H
H
OC
PR₃
G. J. Kubas, Acc. Chem. Res. 21 (1988) 120
M
H
H
M
H
H

$d_{H\text{-}H}$	0.86 Å	0.82 – 0.86 Å
$E_{M\text{-}H_2}$	28 kJ/mol	12 – 40 kJ/mol
$\nu_{H\text{-}H}$	2970 cm^{-1}	2400 – 2800 cm^{-1}

FIGURE 1.6. The bonding of H_2 on a single Ru atom or on a $RuO_2(1\,1\,0)$ surface [26]. (See color insert.)

H_2 molecule leaves both H atoms attached to the central metal atom, with the surface the H atoms prefer to become attached to a neighboring atom into a dihydride configuration.

As far as data are available, with transition metals the metal–metal bond energies are quite similar in cluster compounds and in bulk metals, but—what is even more important—are also comparable to the strength of the chemisorption bond with, for example, CO. In this way, it can be rationalized why the structure of a metal surface is frequently affected by chemisorption.

Theoretical description of the chemisorption bond and calculation of adsorption energies are nowadays mainly based on application of density functional theory (DFT) [28]. This approach has developed to a computational strategy of comparable accuracy to the traditional correlated quantum chemical methods, but at much lower costs, and is now widely used to calculate bond energies to fairly high accuracy comparable to experimental data [29], but sometimes also at variance [30].

1.3. KINETICS OF CHEMISORPTION

Upon adsorption the coverage of the surface by the adsorbate changes, where the *absolute* coverage Θ is defined as the ratio of the density of adsorbed particles n_a to the density of surface atoms in the topmost layer n_s, $\Theta = n_a/n_s$. Saturation equals only in rare cases $\Theta = 1$, so this definition is at variance with the original Langmuir picture [31] assuming that each surface atom represents an adsorption site. This fact is taken into account by introducing the *relative* coverage $\delta = \Theta/\Theta_{sat}$, which then reaches 1 at saturation.

The flux of particles impinging on the surface per cm^2 per second is given by

$$f_s = \frac{p}{\sqrt{2\pi m k_B T}}$$

where p is the pressure (Pa), m is the mass of the incident particle (kg), k_B is Boltzmann's constant, and T is the absolute temperature. As a rule of thumb, 1×10^{-6} Torr impinging on the surface for 1 s would suffice to completely cover the surface if each particle striking the surface is adsorbed. The exposure of 10^{-6} Torr s is denoted as 1 L (Langmuir).

Only in rare cases each particle striking the surface will become adsorbed, but only a fraction s, called the sticking coefficient. Generally, s will decrease with increasing coverage from its initial value s_0 in the simplest (Langmuir) case of nondissociative adsorption as $s = s_0(1 - \delta)$. This is the simplest case that assumes that whenever a particle strikes an empty site it will be adsorbed with probability s_0, otherwise it is reflected and the adsorbates are randomly distributed on the surface.

An extension of this approximation is the so-called "precursor" model [32,33], which is illustrated in Fig. 1.7. This model assumes a finite lifetime of particles in a second layer on the top of the chemisorbed phase ("extrinsic precursor") during