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Catalysis and corrosion: the theoretical surface-science context

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Abstract

NNumerous experiments in ultra-high vacuum as well as ($T = 0$ K, $p = 0$) theoretical studies on surfaces have been performed over the last decades in order to gain a better understanding of the mechanisms, which, for example, underlie the phenomena of catalysis and corrosion. Often the results achieved this way cannot be extrapolated directly to the technologically relevant situation of finite temperature and high pressure. Accordingly, modern surface science has realized that bridging the so-called pressure gap (getting out of the vacuum) is the inevitable way to go. Of similar importance are studies in which the temperature is changed systematically (warming up and cooling down). Both aspects are being taken into account in recent experiments and ab initio calculations.

In this paper we stress that there is still much to learn and important questions to be answered concerning the complex atomic and molecular processes which occur at surfaces and actuate catalysis and corrosion, although significant advances in this exciting field have been made over the years. We demonstrate how synergetic effects between theory and experiment are leading to the next step, which is the development of simple concepts and understanding of the different modes of the interaction of chemisorbed species with surfaces. To a large extent this is being made possible by recent developments in theoretical methodology, which allow to extend the ab initio (i.e., starting from the self-consistent electronic structure) approach to poly-atomic complexes with 10,000 and more atoms, time scales of seconds, and involved statistics (e.g., ab initio molecular dynamics with 10,000 and more trajectories). In this paper we will

1. sketch recent density–functional theory based hybrid methods, which bridge the length and time scales from those of electron orbitals to meso- and macroscopic proportions, and
2. present some key results on properties of surfaces, demonstrating their role in corrosion and heterogeneous catalysis. In particular we discuss
   - the influence of the ambient gas phase on the surface structure and stoichiometry,
   - adsorbate phase transitions and thermal desorption, and
   - the role of atoms' dynamics and statistics for the surface chemical reactivity.

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1. Introduction

1.1. The cutting edge

Surfaces are the cutting edge of material sciences, i.e., a surface is the place where molecules from the gas phase or a liquid come into contact with a material, and where chemical bonds of these approaching molecules may be cut and new bonds formed. If we look around, everything we see is surfaces, and to understand the properties of materials, to understand how materials can be produced, how they can be grown, why and how they corrode or rust, and to how to protect them, for example, how to make the surface hard, and to understand how catalysis works and how it may be improved,—for all this, one has to understand surfaces.

The processes which occur at surfaces play a critical role in the manufacture and performance of advanced materials. Examples are: electronic, magnetic, and optical devices, sensors, catalysts, and hard coatings. In this paper we will mention only very few examples, i.e., focus on molecular surface processes which rule catalysis and corrosion. We note, however, that the same concepts and methodology also apply to the modeling of dopant profiles, surface segregation, crystal growth, and more.

Obviously, a better knowledge of surface- and interface-physics and chemistry is vital to the way we live, i.e. a better knowledge is necessary to support and advance the high technology which very much determines our life style, and it is needed in order to protect the environment. It is evident that there is still much to learn about the intricate molecular and atomic processes that occur at surfaces. The reason for this lack of understanding is largely due to the length and time scales involved (see Fig. 1). Molecular processes at surfaces proceed on a length scale of 0.1 nm (1 nm = 10^{-9} m), electrons move and adjust to perturbations in the femto- (10^{-15}) second time scale, and atoms vibrate on a time scale of a pico- (10^{-12}) second. However, for surface phase transitions, corrosion, crystal growth, or catalysis, the relevant time scale is of the order of microseconds or even seconds. For example, a single dissociation event takes some femtoseconds, and diffusion over a distance of 10 nm may take a time of the order of several picoseconds. Thus, the combination of the various molecular processes which take part in a catalytic reaction (see Section 1.3) may take about a nanosecond. Clearly, the realization of the surface phenomena mentioned above involve very many such reactions and consequently the "whole concert" takes much longer. Therefore in order to evaluate turn-over rates, for example, one needs to perform a statistical average over many such concerted events, which implies that in total, a theoretical simulation must span a time period of several microseconds. For corrosion (as well as for crystal growth), the typical time period is even longer, i.e., here we are dealing with a phase transition or detachment of atoms which proceed at a speed of about one atomic layer per minute. Thus, we have to go to the meso- or even macroscopic regime (see Fig. 1). Everything is determined

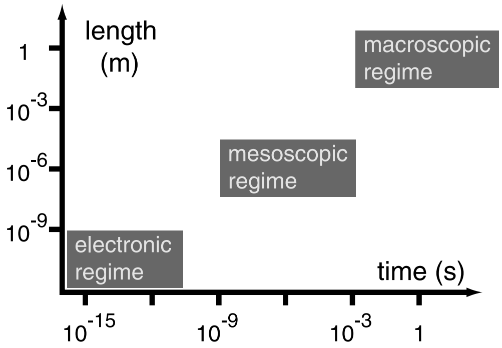

Fig. 1. Schematic presentation of the time and length scales relevant to catalysis and corrosion: The molecular processes, which rule the behavior of a system, proceed in the "electronic regime", but the observable effects only develop after meso- and macro-scopic lengths and times.

by the lower left box in Fig. 1, but how systems evolve and behave is described in the regimes of the other two boxes. The main problem is in the time scale, where we have to bridge 12 orders of magnitude: from 10^{-12} s to seconds. Obviously there is no way that this can be done appropriately by simply using more powerful computers. Not even in 100 years do we expect that this will be possible.

In fact, even if it were possible to perform calculations for the meso- and macroscopic regimes by brute force using electronic-structure theory, i.e., by enlarging the lower left box of Fig. 1, it would not be of much help. The nature of the physics is different in the different regimes: In the lower left box we are dealing with the nature of the chemical bond, and this describes the behavior of the electrons and the interactions between atoms and molecules. However, the other regions are governed by the electronically determined microscopic parameters plus the laws of thermodynamics and statistical mechanics. The electronic regime tells us what can happen. However, whether a process found in this regime is actually relevant for the full concert of possible molecular processes will be decided by the physics in the other regimes. If one likes to understand what it is that determines real-life phenomena, one has to combine (hopefully seamlessly) electronic-structure theory with a proper treatment of statistical mechanics. And this is what we will emphasize and describe in this paper.

The physics of the lower left box of Fig. 1, i.e. the electronic regime and molecular processes, is best described by density-functional theory (DFT) [1–3]. DFT has developed into the most successful and wide-spread approach for accurately calculating and predicting various physical properties of a wide range of materials systems including molecules, bulk solids, and surfaces (see e.g. Ref. [4] and other contributions in that volume). It is called a "first-principles" theory, which in Latin reads "ab initio". For practical calculations it means that everything is evaluated by starting from a self-consistent electronic-structure calculation.

In order to describe the properties and performance of "real materials", as for example those involved in catalysis and corrosion, one has to go beyond the electronic-structure calculations. For this second step, four different methods have been developed, which apply to different situations:

- If it is necessary to follow the motion of the atoms in detail, ab initio molecular dynamics is used [5,6]. Here ab initio refers to the fact that the forces acting on the nuclei are calculated by DFT. And then the atoms are allowed to move, being accelerated by the ab initio forces as described by Newton's laws [7,8]. For atoms heavier than hydrogen, the nuclear motion is indeed classical—within the required accuracy—and thus, the ab initio molecular dynamics treatment is appropriate [6].
- For systems which involve hydrogen, an ab initio quantum dynamics approach has been developed. Here a Schrödinger equation is also solved for the nuclei, where the potential energy entering the Hamiltonian is the DFT total energy [6,9–11]. Thus, zero-point vibrations and tunneling are allowed. In Section 3.3 we give an example of what can be learnt from such studies. Other examples are given in the paper by Groß in this volume.
- Often processes are close to thermodynamic equilibrium. Then it is e.g. important to consider the possibility of exchanging atoms with the environment. When it comes to a description of surface segregation, adsorbate phase transitions as a function of temperature, and even as a function of heating (time dependent change of temperature), a lattice-gas Hamiltonian approach is appropriate (e.g. Ref. [12]), which enables us to evaluate the partition function, and, of course, from the partition function all thermodynamic potentials can be obtained. In Section 2 we give two examples of thermodynamic equilibrium and/or close to thermodynamic equilibrium studies relevant to the context of this paper.
- For systems which are not in thermodynamic equilibrium, but which are determined by the dynamics of the atoms, and when the time scale is beyond that possible in the direct molecular dynamics calculations, the appropriate method

> is the kinetic Monte Carlo (kMC) approach [13]. This employs statistical sampling of the various adparticle surface processes and brings us into the time regime of seconds and minutes. Corrosion, crystal growth, and also catalysis are examples for which this approach will be useful. In Section 4 we describe the state-of-the-art of this method.

One may argue that using a different methodology for different types of problems lacks elegance and beauty. Admittedly this is true, i.e., the choice of methodology is done pragmatically. It is taken because we like to obtain understanding. In fact, we believe that "one theory for everything" is an irrational fiction. What is needed is understanding, as we have advocated before [4], and this requires knowledge about various areas: electronic-structure theory, condensed matter physics, material science, chemistry, computer science, thermodynamics, and statistical mechanics. In other words, this field is very interdisciplinary in nature, which, besides curiosity, makes it appealing and fascinating.

In the present paper, we concentrate on metal and metal-oxide surfaces, and do not e.g. discuss zeolites, the use of which as catalysts represents an area of its own. Zeolites have properties that may not undergo a significant change at high pressures and temperatures, instead, other factors play a role in their activity such as the geometry of the cages, pores, and channels. Hence, this material class lies outside the emphasis of the present paper and we refer the interested reader to the contribution by Sinfelt in this volume. The remainder of this paper is organized as follows. In Section 1.2 we summarize the main concepts and definitions behind heterogeneous catalysis and corrosion. Then in Section 1.3 we extend this description by discussing the various molecular processes, which happen at surfaces and rule, though in a concerted and statistical manner, catalysis and corrosion. In Section 2 we describe concepts (and results) for a surface under realistic conditions, i.e., when it is in contact with a realistic atmosphere at finite temperature and pressure. In Section 3 we discuss the asymptotic interaction of atoms and molecules at, and with, surfaces (reactivity theory); it describes the nature of the chemical bond at the transition state of a surface chemical reaction (Section 3.2), and it emphasizes the importance of the dynamics and statistics for a proper account of surface reactivity (Section 3.3). We discuss in Section 3.4 the importance of an optimum adparticle–substrate bondstrength in relation to its reactivity and describe examples of how it can be modified either by adjusting the coverage or through electronic excitation. Then in Section 4 we describe how the various individual molecular processes could be combined and the statistics taken into account. That is, we show how the full concert of a sustained catalytic process as well as corrosion could be treated. This section describes work in progress and is pointing towards future theoretical work. In this way it contains the outlook and concludes the paper.

1.2. Concepts and definitions of heterogeneous catalysis and corrosion

A "catalyst" is a substance that enhances the rate at which a certain chemical is produced, possibly it also reduces the rate of another competing reaction. And a catalyst does this without being consumed in the process. Then "catalysis" is the phenomenon of a catalyst in action. A heterogeneous catalytic reaction is a concert of processes whereby the word "heterogeneous" refers to the situation that the net reaction occurs when reactants and catalyst are present in different phases. The catalytic reaction between adsorbed particles exhibits a free-energy barrier which is lower than that of the chemical reaction between the reactants in the gas phase. The result is that the reaction is kinetically accelerated. We refer to Ref. [14] for a comprehensive publication on heterogeneous catalysis. Fig. 2 gives a schematic example of a gas phase reaction (left) and how it is changed by a catalyst (right). Catalytic reactions at surfaces have traditionally been classified as different types: a so-called "Langmuir–Hinshelwood" reaction is where the reactants are both adsorbed on the surface prior to reaction; this is the most usual case in heterogeneous catalysis. An "Eley–Rideal" reaction mechanism is where the chemical reaction takes place between a gas phase particle (e.g. CO)

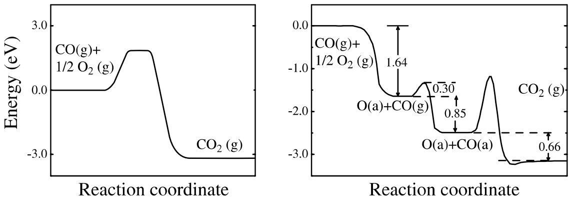

Fig. 2. Schematic illustration of the energy diagram of a simple gas phase reaction, using the CO oxidation as an example (left) and the corresponding reaction over a catalyst (right). In this reaction, the CO molecule interacts with an O atom, either from the O_2 molecule (left) or with an adsorbed O atom (right), to form carbon dioxide, CO_2. The rate for crossing energy barriers is $\Gamma = \Gamma_0 \exp(-\Delta E/k_B T)$, where Γ_0 is the attempt frequency, ΔE the height of the energy barrier, k_B is Boltzmann's constant and T is the temperature. Note that the energy scales of the left and right figures differ by a factor of two. Obviously, the catalyzed reaction is much more efficient. Labels (g) and (a) denote "gas phase" and "adsorbate". (Right figure from Ref. [16].)

which scatters at an adsorbed particle (e.g. O). Thus, the reaction product (CO_2) is formed during a scattering event. This reaction mechanism is usually assumed to be un- or less-likely because the number of gas phase particles hitting the surface per site per second, at a given temperature and pressure is typically low compared to the attempt frequency of two particles already adsorbed on the surface in the case of the Langmuir–Hinshelwood process. The classification of these two types of reaction mechanisms was originally put forward by Langmuir [15]. Finally, for oxidation catalysis over metal oxides, a frequently considered assumption is that the required oxygen is taken out of the oxide material, which is called the "Mars–van Krevelen" mechanism.

In industry, catalytic substances (such as transition metals) are typically utilized as a highly dispersed catalyst on a "support material". This is for a number of reasons: firstly, to increase the available surface area for reaction; support materials should thus have a high surface area, be durable, and inexpensive. Second, the interaction of the dispersed catalyst with the support can lead to an enhanced chemical efficiency compared to reaction over the catalytic material alone, as for example, in the case of some catalytic nanoparticles. Finally, transition metals are expensive and limited in supply; already in 1991, 87% of the world demand of Rh went to catalysts [17].

The nature of the surface, which is exposed to the reactants, is crucial. However, the knowledge about the surface, as it develops under the actual catalytic conditions, is typically uncertain, and we believe that many of the "established" ideas and concepts are incomplete, and some may be wrong. Two examples are briefly mentioned to illustrate this point. Oxidation catalysis at a ruthenium catalyst probably does not take place at the Ru metal, initially introduced as "the catalytic material". Instead, under normal (or high) pressure and high temperature conditions, the Ru metal undergoes a phase transition into a mesoscopically structured system with areas of very different behavior, which most likely can be characterized as oxygen adsorbate regions, RuO_2 oxide regions, and other (strained) Ru oxides [18–20] (see also the discussion in Section 4). We believe that the coexistence of the different regions is crucial for understanding catalysis. But we also note that this is not an accepted or widely shared view, and "standard" surface-science studies on single crystals are often discussed in terms of their direct significance for catalysis. The other example is the dehydrogenation of ethylbenzene ($C_6H_5CH_2CH_3$) to form styrene ($C_6H_5CH{=}CH_2$) using potassium promoted iron-oxide catalysts. Recent work surprisingly shows that after the "induction period" (see below) ethylbenzene apparently does not interact with the iron oxide and thus the catalytic activity is in fact not related to iron oxide; rather the catalyst is a "new material" that is created during initial stages of the interaction of ethylbenzene with the iron-oxide surface: It seems that the catalytically active material (for styrene formation) is a certain type of carbon [21]. In relation to the nature of surfaces under actual catalytic conditions, we mention that industrial catalysts typically require an induction period, i.e. a time to get into efficient action (sometimes of hours, or days) before performance reaches steady state, which indicates that the native catalyst material initially undergoes significant changes in its surface structure and/or composition. We believe that most (maybe all) catalysts which exhibit an induction period may undergo such dramatic

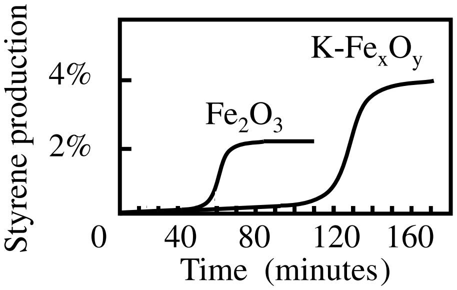

Fig. 3. Induction period of styrene production from ethylbenzene (EB) using hematite (Fe_2O_3) and a potassium-promoted iron-oxide catalyst. The plot is schematic, but based on data of Ranke and coworkers [21,22], who used a 1 cm^2 sized model-catalyst under near-industrial conditions ($T = 870$ K, $p_{EB} = 3$ mbar, and the ratio of EB to water steam is 1:10).

changes and we expect many more surprises, of similar significance and impact as that of the above mentioned "promoted iron-oxide catalyst". Fig. 3 illustrates this point for styrene production which shows the required induction period where an iron-oxide catalyst is used. A similar, but longer induction period occurs for the K-promoted iron-oxide catalyst, which results in a higher formation rate of styrene. (We note that in Fig. 3 the rate is low because the size of the catalyst used in this study is small (1 cm^2). Industrial reactors consist of catalyst-filled tubes that are several meters long, and then the rate is about 50%.)

The behavior of a catalyst under ultra-high vacuum (UHV) conditions (10^{-13}–10^{-9} atm) and low temperatures (e.g. room temperature and below) may be different from the behavior at high pressures and temperatures, and this is called the "pressure gap". In this respect, one of the main concerns in catalysis research has been whether it is possible to extrapolate between the UHV conditions and single crystal substrates of surface science, to the high pressures and temperatures, and the often quite complex structures of industrial catalysts under reaction conditions. This deviation between the single crystals and "working" catalyst materials, has been coined the "material gap". Because the native catalyst material may undergo significant changes when under actual operating conditions, the material and pressure gaps are typically linked (see e.g., the contribution by Zaera in this volume). Another aspect is that in real catalysis the support material may play a more significant and different role than often assumed, and this support material, as well as the interface between nanoparticles and the support, may be substantially different under realistic catalytic conditions than in hitherto performed UHV studies.

We also note that industrial catalysis involves more aspects than those mentioned above and in Section 1.3. For example, there is "selectivity", which means that only the desired reaction should take place, and competing reactions yielding unwanted products are suppressed. Sometimes this is the main problem; for example, in ammonia synthesis the dissociation of nitrogen is the rate-limiting step, and for the cracking of large hydrocarbon molecules into smaller ones, which is a crucial process in the petroleum industry, the catalyst must actuate scission of the carbon–carbon bonds. Also the buffering of intermediate chemical products is important, as is the self-maintenance of the catalyst. And often it is important that no poisonous by-products are released. Furthermore, the role and mechanisms of promoters and poisoners are very important but are rarely well understood. In order to enhance the performance of a catalyst, various atomic species are sometimes added to the catalyst. These additives are called modifiers and if it is a "good modifier", that is, if it brings about an improvement in the performance of the catalyst, then it is termed a "promoter". Conversely, a "bad modifier" is referred to as a "poison". Usually additives are deliberately introduced but sometimes they arise unintentionally through contaminents. The economic importance of catalysis for creating desired substances is significant; but perhaps even more important is that catalysis is necessary for preserving the environment. The catalytic converter to clean the automotive exhaust (i.e. convert CO to CO_2) is just one example.

Corrosion has a similar economic importance, but, in contrast to catalysis, it is unwanted. Corrosion can take place in different environments such as in the atmosphere, in solution, and in soil. Most metals are thermodynamically unstable in aqueous environments, and their corrosion in water or an electrolytic solution, made by dissolving a salt, acid, or base in water, is an electrochemical process where the basic mechanism involves removal of valence electrons from the metal atoms which become ions that move into the solution, and then often more stable compounds such as iron oxide (e.g., rust) may form. This basic mechanism is called an "anodic reaction", and for the corrosion process to proceed there must be a corresponding "cathodic reaction" that accepts the electrons. We discuss this in more detail in Section 1.3. Corrosion of a metal brings the metal to its thermodynamic ground state under the existing environmental conditions. Fig. 4 illustrates this point by giving the energetics of the formation of an iron-oxide layer on iron due to the interaction of O_2 with Fe. Often metal oxides are insulators, but RuO_2, for example, is metallic with a conductivity comparable to that of copper [23]. Obviously, corrosion compounds start to form on the surface as thin films, and if they are hard and impenetrable, and if they adhere well to the material, the progress of corrosion will stop (or be significantly slowed down) after a typical thickness of the order of 2–5 nm. This is then known as passivation. For example, a reactive metal like iron, which corrodes at half a millimeter per year in salt water, corrodes a thousand times slower in environments that allow the formation of a passive film.

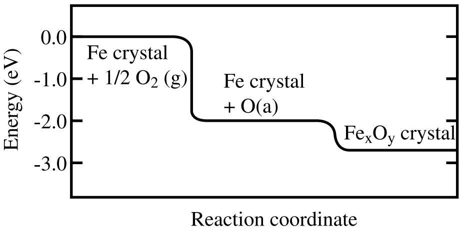

Fig. 4. Schematic energy diagram of metal corrosion, for the example of O_2 at an Fe surface, that illustrates the point that corrosion processes lower the energy of the metal/environment system as far as possible, through the formation of more stable structures: In an O_2 atmosphere the metal oxide (Fe_xO_y) is thermodynamically more stable than the metal, but typically, the oxide layer formed at the surface prevents the phase transition being completed. The "reaction coordinate" on the horizontal axis represents, in a general way, the atomic positions of the atoms involved in the reaction.

In order to try and help protect the metal from corrosion through passive film formation, an alloying element can be added, for example, chromium to iron to form stainless steel. (A most common stainless steel is comprised of iron with 18% Cr and 8% Ni, but other elements may also be added in smaller quantities such as Mo, Se.) Apparently, the addition of chromium has the result that the surface-oxide film formed is more resistant to breakdown. We point out that as yet there is not a good quantitative understanding of how chromium makes stainless steel stainless, but it is thought that the Cr in Fe segregates to the surface and covers the surface with chromium oxide. Chromium and aluminum form the most stable and protective of such films. The films that form on copper and iron as a result of corrosion are known as tarnish and rust, respectively. The corrosion resistance of a passive film is determined by its ionic and electronic transport properties, which are largely determined by the film's crystallographic structure, defects, and its microstructure. In general, the atomic structure of such oxide films is still poorly understood. We like to note, however, that a recent in situ X-ray diffraction study of the passive film on iron that forms in aqueous solution, which has been an outstanding question for decades, concluded that it is a highly defective nanocrystalline spinel oxide with a high concentration of vacancies and interstitials [24,25]. Clearly, there is much quantitative and interesting work to be done in this field.

Like catalysis, understanding of the various molecular processes involved in corrosion encompasses concepts from a variety of disciplines, including thermodynamics, electrochemistry, physical metallurgy, condensed matter, and statistical mechanics. The adsorption of reactants on the surface (atoms or molecules from the environment) represents the first elementary step in corrosion (and in a catalytic reaction cycle). Thus, understanding the chemisorption step (bond breaking or weakening in the reactant and the making of new bonds to the surface) has been (and still is) one of the prime goals. The main aspects that have been addressed by theoretical surface scientists, in particular, are the atomic and electronic-structure, the binding energies of atoms and molecules on metal surfaces and the nature of the bonding, activation energies, and diffusion at the surface and from the surface into the bulk. In addition, factors such as temperature, gas phase pressure, etc., namely, the chemical and thermal contact with the environment can play a decisive role in the behavior of the system so that it is also desirable to take it into account. Furthermore, often interesting phenomena occur far away from equilibrium so that in order to understand such processes, it can be necessary to go beyond ground state and equilibrium properties. We will discuss some of these aspects in this paper, and some are still waiting to be treated properly (see Section 4).

1.3. Molecular processes relevant to heterogeneous catalysis and corrosion

In this section we describe important molecular processes which are part of corrosion and heterogeneous catalysis and which will be drawn upon in subsequent sections in discussing selected examples of recent studies. Understanding of these individual processes is crucial, but we also emphasize that in the end what counts is how they act together, and it is the statistical sampling that determines which of these processes are really relevant. The main molecular processes are:

- the adsorption of atoms and molecules (often dissociatively) on a solid surface from the gas or liquid phase,
- diffusion on the surface,
- diffusion of adsorbates into the subsurface region and of substrate metal atoms (or ions) through a surface-oxide layer (if the latter is present),
- interactions between different adparticles at the surface,
- chemical reaction of different adparticles,
- desorption of the reaction product.

In Fig. 5 we illustrate some of these molecular processes, referring to the interaction of Ru with O_2: Molecules present in the gas phase may bond to the surface in a molecular form or may dissociate into atoms depending on a number of factors such as the temperature and pressure at which adsorption takes place, surface structure, and the extent to which the surface is covered by adsorbate

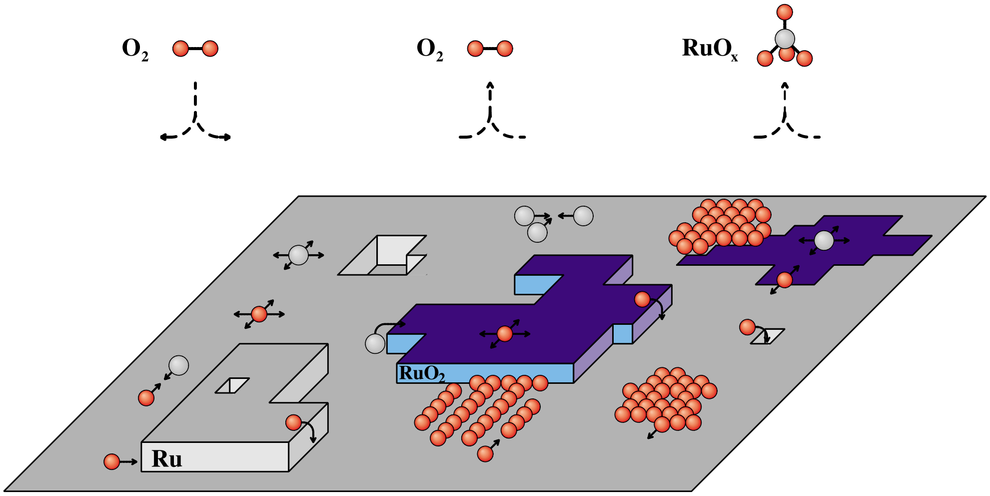

Fig. 5. Schematic illustration of some microscopic atomic and molecular processes that take place at surfaces and which are relevant for heterogeneous catalysis and corrosion. The example substrate here is ruthenium in an oxygen environment. For example, oxygen molecules, O_2, may dissociatively adsorb on the surface (indicated by the down and outward arrows), the O atoms may diffuse on the surface (as indicated by small circles with arrows), and may associatively desorb into the gas phase as O_2 (indicated by the upward and inward arrows). Alternatively they may react with the Ru atoms of the substrate to form islands of ruthenium dioxide, RuO_2, or may desorb as RuO_x molecules.

species. These adparticles then diffuse around on the surface and may cluster together forming islands, or they may react with other adsorbed species to form a molecular product that desorbs from the surface, or to form a new phase that stays on the surface, e.g. an oxide. Furthermore, surface segregation of metal cations may occur. In heterogeneous catalysis and corrosion, almost always one of the approaching molecules dissociates and it is the availability of bonding sites on the substrate that affords and favors the catalytic or corrosion process.

With respect to corrosion in solution, we elaborate a little further below on some of the typical reactions and processes that take place and compare with the case of corrosion in a pure gas environment. Here the examples are iron in water (which contains oxygen) and in a pure oxygen atmosphere. Corrosion reactions that do not involve water or aqueous solutions are often called "dry" corrosion reactions and those that do are often called "wet" corrosion reactions. Firstly, we point out that corrosion can be viewed as a heterogeneous chemical reaction at a metal/non-metal interface in which one of the reactants is the metal itself, and the non-metal reactants are the environment. One of the reaction products will always be an oxidized form of the metal and the other a reduced form of the non-metal. For example, non-metal reduction reactions may be $O_2 + 2me^- \rightleftharpoons 2O^{m-}$, $OH + e^- \rightarrow OH^-$, $H^+ + e^- \rightarrow (1/2)H_2$. We illustrate these dry and wet corrosion processes in Fig. 6, left and right, respectively. For the dry reaction, which typically requires elevated temperatures, the metal/oxide and oxide/gas interfaces can be regarded as the anode and cathode, respectively. We recall from Section 1.2 that the anodic reaction involves loss of valence electrons and creation of metal cations (e.g. $Fe \rightleftharpoons Fe^{z+} + ze^-$) and the cathodic reaction is one that accepts the electrons; here it is the ionization of O_2 to form adsorbed, negatively charged O atoms at the surface (e.g., $(1/2)O_2 + 2e^- \rightleftharpoons O^{2-}$). The chemisorbed O atoms cause a high electric field so the system tries to lower it by either "pulling" metal ions from the metal or "pushing" oxygen ions into the metal lattice (segregation and diffusion). This mass transport enables the formation of the corrosion product, i.e. the metal oxide formation, which as we showed in Fig. 4 for the example of iron oxide, has a lower energy than that of clean Fe in such an environment. In the wet case, the anodic reaction is the same, except that the metal ions diffuse into the solution. This sets up an electric potential difference between the metal and the solution and charge separation occurs. The electrons lost from the metal atoms may react with the water and oxygen to form OH^- ions ($O_2 + 2H_2O + 4e^- \rightleftharpoons 4OH^-$) or with protons to form hydrogen ($2H^+ + 2e^- \rightleftharpoons H_2$). (The protons being formed via e.g. $Fe^{2+} + H_2O \rightleftharpoons FeOH^+ + H^+$.) These latter two reactions, together with the anodic reaction, represent the standard "dissolution process". The OH^- ions can react with the metal cations, e.g., to form ferrous hydroxide $Fe(OH)_2$ for the case of iron, which might oxidize to form ferric hydroxide, $Fe(OH)_3$, and as a final product, the well known reddish brown rust, $Fe_2O_3 \cdot H_2O$ of which there are several varieties (i.e. hydrated iron, where each molecule of iron oxide is chemically bound to one or more water molecules). If there is insufficient oxygen, Fe_3O_4 or α-Fe_2O_3 may form [26].

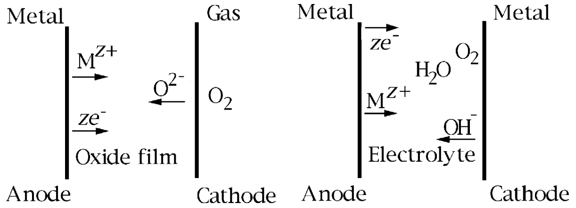

Fig. 6. Schematic diagram illustrating the interaction of a metal with dry, O_2, (left) and wet, e.g. $O_2 + H_2O$, (right) environments, and some of the mechanisms that give rise to the formation of the passive oxide layer and the effective anodes and cathodes. In the former case the metal atoms lose valence electrons (ze^-) and become cations (M^{z+}). This is the anodic reaction and can be regarded as occurring at the metal/oxide interface. The electrons are accepted by oxygen to form negatively charged O atoms at the surface; this is called the cathodic reaction and can be thought of as taking place at the oxide/gas interface. In the wet case (right), the anodic reaction is the same except that the metal ions diffuse into the electrolyte. The electrons lost from the metal atoms may react with the oxygen and water to form, e.g., OH^- which may react with the cations to form the oxide product.

In Fig. 7 we illustrate in more detail some of these microscopic steps that occur in the building-up of the films. The film structure of Fe in an O_2

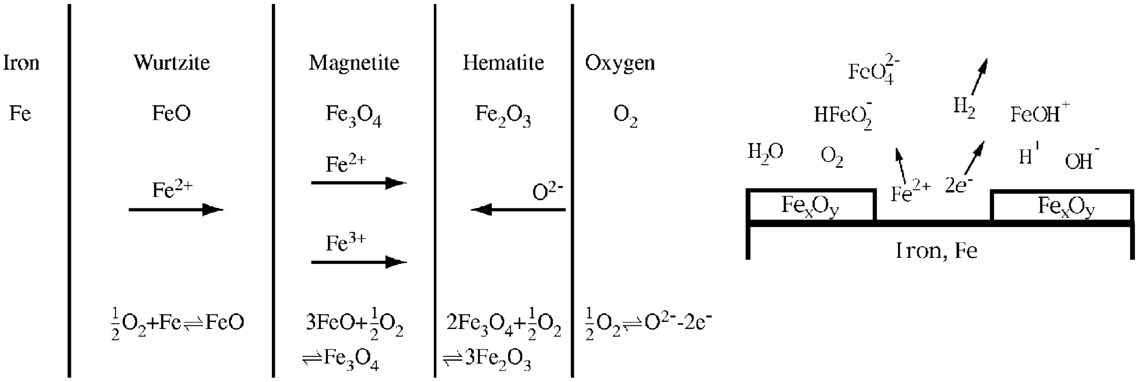

Fig. 7. Illustration of the formation of iron oxide in (left) an oxygen gas environment (for temperatures greater than about 570 °C) showing the different states of oxidation of the film (FeO, Fe_3O_4, Fe_2O_3) and (right) in the vicinity of an imperfection or pore at an iron surface which is immersed in an aqueous environment containing water and oxygen. In the latter, reactions at the pore (bare Fe surface) present either anodic or dissolution processes, while those on the oxide surface are cathodic in nature. Besides water, H_2O, and oxygen, O_2, metal ions, Fe^{2+} and electrons, $2e^-$, some of the molecular reaction products are illustrated. (Various solid compounds also form as mentioned in the text, but are not explicitly shown for simplicity.) The left figure is a simplified form of that given in Ref. [27].

environment is believed to consist of oxide layers of different stoichiometries: initially, at sufficiently high temperatures (>570 °C) a (wurtzite) FeO layer forms on the surface, which, with further oxidation, leads to growth of Fe_3O_4 and Fe_2O_3 (see Fig. 7, left). We refer to Refs. [28,29] for a discussion of theories of the initial oxidation of metals and some recent results. In the wet environment (Fig. 7, right) we illustrate how quite naturally the corrosion processes can occur at an imperfection in the surface (e.g. a pit or pore exposing clean Fe). A local anode and cathode are formed where the bare Fe acts as the former and the developing oxide as the latter. Some of the characteristic reactions and reaction products are shown. In the present paper our subsequent discussions relate more to the case of dry corrosion processes.

2. Surfaces in or close to thermodynamic equilibrium

When a surface is in contact with a realistic environment, e.g. an atmosphere containing oxygen and water, atoms or molecules from the environment can adsorb on the surface and/or atoms from the surface can be released into the environment. What is typically called a stable surface structure is in fact a statistical average over adsorption and desorption processes. The surface composition and geometry which is assumed in thermodynamic equilibrium depends on the type of environment, e.g. the partial pressures of O_2 and H_2O and temperature. Considering, for example, iron oxide in thermodynamic equilibrium, the energy to take an oxygen atom out of the bulk, or out of the surface, or out of a gas phase O_2 molecule, or out of a gas phase H_2O molecule is the same. This equality, as exemplified for the oxygen atom, is in fact the definition of thermodynamic equilibrium, and if the chemical potentials of a certain species in different coexisting phases were not the same, the system would change, e.g. by altering the surface geometry or composition, until thermodynamic equilibrium is reached. This process can be slow and kinetically hindered, and corrosion is one example where kinetic hindrance stops oxidation if a passive film forms and has attained a certain thickness. Thus, under these circumstances the corrosion compound which forms on a metal surface is not in thermodynamic equilibrium with the metal bulk. However, the surface (at least at not too low temperatures) is likely to be in thermodynamic equilibrium with the ambient atmosphere.

Knowledge of the surface composition and geometry is a prerequisite for describing catalytic processes and corrosion or passivation. In Section 2.1 we show that (and why) UHV surface science, and also low pressure studies, are likely to investigate a surface which is significantly different in its chemical activity and properties to that which is actually assumed when the surface is in contact with a realistic atmosphere. Then in Section 2.2 we describe how the temperature and pressure dependence of adsorbate phases can be treated theoretically, with periodic as well as disordered surface structures. As an example of this approach we present an ab initio calculation of temperature programmed desorption, appropriate for not too fast heating rates so that the surface structure can always assume the thermal equilibrium surface geometry.

2.1. The role of the ambient atmosphere

For metal oxides [30] (and this includes the oxide film which develops at a metal surface under realistic conditions) the understanding of the surface terminations (composition and atomic geometry) is still very shallow. The reason is that electron scattering and spectroscopy techniques and scanning tunneling microscopy (STM) are hampered by the insulating nature of the material. Also theoretical studies for metal oxides are very demanding because they have to deal with a rather open structure, oxygen with very localized wave functions, huge atomic relaxations, big supercells, and often, as for example in iron oxide, 3d electrons and magnetism. In this section we describe concepts and some recent theoretical work on atomistic thermodynamics of metal oxides in contact with a realistic liquid or gas phase. We start with α-Fe_2O_3 (hematite) in an oxygen atmosphere, and at the end we add some words about α-Al_2O_3 (corundum, or sapphire) and the changes which occur, when in addition to O_2 also hydrogen (either in the form of H_2 or water) is present in the environment. While Fe_2O_3 may be a possible catalyst, Al_2O_3 is a frequently used support material.

Before 1998, theoretical work had concluded that the most stable surface structure of α-Fe_2O_3 was metal terminated, with one Fe atom in the surface unit cell. A termination with three O atoms in the surface unit cell (denoted, O_3) was excluded because it was believed to yield an electrostatic energy divergence. This argument, based on the assumption that a bulk-like geometry is maintained, was supported by some calculations. Recently, Wang et al. [31], however, through detailed DFT–GGA calculations allowing full atomic relaxation and possible exchange of surface atoms with the environment (the O_2 atmosphere acting as a reservoir giving (or taking) any amount of oxygen to (or from) the sample, without changing the temperature or pressure) showed that this is not correct. In particular, by calculating the surface energy for various hypothetical surface terminations as a function of the oxygen chemical potential, which is uniquely determined by the environment (see e.g. Refs. [31,32]), the energetically most favorable structures could be derived for certain conditions. In Fig. 8 we show these results: While under oxygen poor conditions, it can

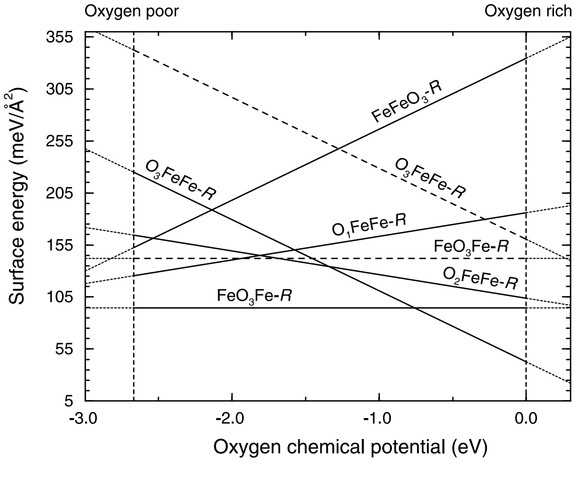

Fig. 8. Surface energies of different $Fe_2O_3(0001)$ surface terminations. The lines are labeled by the sequence of layers from the surface toward the bulk, and $-R$ stands for the bulk-like continuation. The zero of the chemical potential is set to $(1/2)E_{O_2}$, the total energy per oxygen atom of molecular O_2 at ($T = 0$ K). The allowed range of the oxygen chemical potential is indicated by the vertical dashed lines, where the left one corresponds to strongly Fe-rich (i.e., oxygen-poor) conditions, and the right one corresponds to strongly oxygen-rich conditions (i.e., high oxygen gas pressure). Full lines show results for relaxed geometries, and dashed lines give for comparison results for unrelaxed surfaces (after Ref. [31]).

be seen that the most stable surface is indeed the mentioned iron terminated one, however, at higher oxygen pressure, the O_3 terminated structure surprisingly becomes more stable. In fact, the crossing point of the surface energies of these two surface configurations is roughly at room temperature and 1 atm, which implies, that this previously rejected surface geometry may certainly play a significant role. Considering the surface relaxations involved, they are found to be huge (changes of interlayer spacings can be as large as 80% of the bulk value), and the surface electronic-structure, as well as the magnetism are very different to that of a truncated bulk geometry. This may be already guessed from Fig. 8 because the difference between the surface energies of the unrelaxed (dashed lines) and relaxed (full lines) structures is significant (for details see Ref. [31]).

Analogous studies for Al_2O_3 [33] showed that its (0001) surface, when in contact with an O_2 environment, is always Al terminated, in the whole range of accessible oxygen chemical potentials. This difference to the iron oxide is related to the fact that transition metals have more flexible valence states than Al. Interestingly, when in addition to oxygen, also H_2 and H_2O were considered as part of the environment, the surface of aluminum oxide was found to be the O_3 terminated one, where, however, each oxygen also binds an H atom. Thus, we may also say that this surface is OH terminated.

These are just two examples (Fe_2O_3 and Al_2O_3) which show that under realistic conditions surfaces can be very different to those often studied in UHV. The difference can be dramatic, and the electronic properties and performance can have little resemblance to the low pressure results. We like to emphasize this point by also stating that surfaces in general (as compared to the bulk or even to the bulk terminated surface) and in particular as they develop under realistic conditions, represent a new material.

For corrosion that results in passivation of the surface, thermodynamic equilibrium between the film and the substrate is not achieved; the reason that the film stops growing is because of kinetic hindrance. Nevertheless, the film may have a sufficient thickness in order to obtain a rough estimate of the metal-rich (oxygen poor) boundary of the surface structures and the compositions which may develop.

2.2. Surface phase transitions and thermal desorption

For surfaces that are in, or close to, thermodynamic equilibrium and which depend on the atmospheric environment and temperature, such as adsorbate phases which may initiate corrosion and surface phase transitions of a catalyst under high temperature and pressure conditions, and/or to describe surface segregation, an appropriate and general approach to describe the structure and to analyze adatom–adatom interactions as a function of temperature and pressure is a lattice-gas (or Ising) model [34,35]. This approach is quite powerful, and e.g., also enables us to evaluate medium range interactions between different adatoms. Furthermore, the Hamiltonian need not be restricted to the description of adsorbates on a surface; it can, for example, be extended to account for subsurface species, describing their mutual interactions, as well as their interactions with on-surface adsorbates.

This approach starts by defining possible sites for the adatoms, and that this is possible is the main assumption of the approach. Then, in a second step it is determined whether or not these sites are occupied, and there is no restriction that this occupation should be dense or sparse, or periodic, or disordered. From the lattice-gas Hamiltonian one can evaluate the partition function and thus obtain the thermodynamic properties of the system. Furthermore, through combination with rate equations, a description of the kinetics (if it proceeds close to thermodynamic equilibrium) can be obtained, such as thermal desorption.

The lattice-gas Hamiltonian is built-up from the energy of an isolated adatom at a surface including its partition function accounting for vibration perpendicular, and frustrated translation parallel, to the surface. Interactions from possible neighboring adsorbates are then added, for example, two-body or pair-wise interaction energy contributions due to adatoms at nearest neighbor lattice sites, at second neighbor sites, and third neighbor sites etc. Also, three-body (or trio) interactions that account for modifications because the interaction between two adsorbed atoms is changed, when a third adatom is close by can be included, as can higher-order interactions. The number and type of interactions (and atomic species) can be increased at will until it is judged that the Hamiltonian is sufficiently accurate. These quantities can all be obtained from DFT calculations: Specifically, the individual adatom–adatom interactions can be deduced from calculations with different supercells and different adatom geometries by expressing the adatom adsorption energy in terms of its interactions with neighboring adsorbates. When done for the different structures, this yields a system of equations that can be solved simultaneously. Direct calculation of the individual adatom–adatom interactions would not be readily accessible because of too high computational costs.

In what follows, we give an example of this approach for the system of oxygen at Ru(0 0 0 1) where the temperature-programmed desorption of O_2 is calculated in the coverage regime from low coverage to a full monolayer [36]. Temperature-programmed desorption is one of the most widely used experimental techniques for studying the binding energies of adsorbed species. In this experiment one prepares an adsorbate layer of a given initial coverage at a given temperature and measures the desorption rate of the particular species as a function of increasing temperature. The rate depends exponentially upon the negative of the activation energy barrier for desorption, which in turn is also a function of the coverage. The prefactor to the exponential involves a sticking probability (as will be discussed in Section 3.3). The lattice-gas Hamiltonian constructed in this study [36] used two-body interactions up to third neighbor distances and three types of three-body (trio) interactions. Also two types of adsorption sites were included, namely, the hcp- and fcc-hollow site, and also interactions between the O atoms in these two types of hollow sites were included up to third neighbor distances. The calculated interaction parameters agree well with those determined recently from STM studies [37]. Quantitative information on adsorbate–adsorbate interactions have also been obtained for nitrogen on Fe(1 0 0) from STM investigations [38].

In Fig. 9 we show the theoretical temperature programmed thermal desorption spectra for O_2, which is compared to recent experimental data [39]. It can be seen that the theoretical spectra agree well with the experiment, in particular the shift of the peak maxima to lower temperatures for higher initial coverages which is due to repulsive adsorbate–adsorbate interactions. The structure (e.g. the various shoulders) in the calculated TPD spectra is due to the formation of ordered phases.

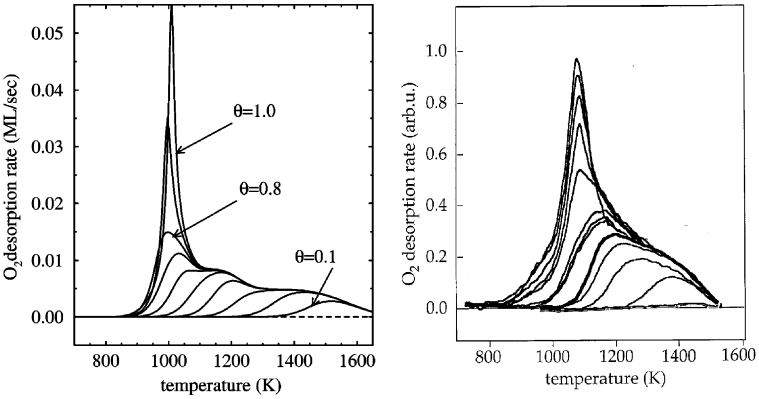

Fig. 9. Theoretical (left panel) and experimental (right panel) temperature programmed desorption curves (heating rate of 6 K/s). Each curve shows the rate of oxygen molecules that desorb from the Ru(0 0 0 1) surface as a function of temperature when the system is prepared with a given initial oxygen coverage. The initial coverages are reflected by the area under the curve. For the theoretical results initial coverages are 0.1–1.0 ML in steps of 0.1; the experimental results also span this coverage region (from Ref. [36]).

The presence of such phases can be predicted by calculation of the isosteric heat of adsorption (the energy which an O_2 molecule gains by dissociatively adsorbing on the surface) as a function of coverage, which was also presented in Ref. [36]. From the calculated isosteric heat of adsorption, stable structures of O on Ru(0 0 0 1) were identified for coverages 1/4, 1/2, 3/4, and 1 ML which correspond to each of the ordered phases that form in nature, namely, (2×2)-O, (2×1)-O, (2×2)-3O, and (1×1)-O [36]. We note that similar first-principles based approaches have successfully been used for studying bulk phase diagrams [40,41]. Also, recently the lattice-gas Hamiltonian, together with the kMC approach has been used to study the diffusion and island nucleation at metal surfaces [42].

3. Reactivity theory

In the catalytic synthesis of ammonia, for example, it is the dissociative adsorption of N_2, which largely determines the turn-over rate (see e.g., the contribution by Sinfelt in this volume), and for various examples of oxidation catalysis it can be the dissociative adsorption of O_2. In "catalytic cracking" where large hydrocarbon molecules are decomposed into smaller ones, it is necessary that the catalyst breaks the carbon–carbon bonds. And also for corrosion it is necessary that molecules from the environment dissociate in order to take part in the formation of the corrosion compound. In general, the ability of a surface to break bonds of an approaching molecule is referred to as the surface reactivity. And this aspect will be discussed in the following three subsections. We also mention that it will often be important to specify the surface reaction to which the "surface reactivity" refers (e.g. H_2 dissociation and O_2 dissociation can be quite different at the same surface).

In gas phase chemistry "reactivity indices", based on the analysis of the electronic structure of reactants before they interact, have been useful. In Section 3.1 we give a brief summary of these ideas, but then we will stress (in Section 3.2) that the interaction of molecules at surfaces is typically quite strong and therefore will often fall outside the applicability range of "reactivity indices". And in Section 3.3 we discuss the importance of the statistics of the dissociation dynamics, demonstrating this point with an example showing that at low temperature palladium has the same surface reactivity as rhodium, although from the electronic structure Pd should be much less reactive.

3.1. The static, asymptotic behavior (reactivity indices)

The description of the early stages of a chemical reaction, i.e. when the interaction between the reactants is still weak, may be characterized by the so-called reactivity indices. These are given by the changes in the electronic structure of a reactant (before the reaction takes place) as stimulated by an external perturbation. It was Fukui [43,44], who taking notice of the principal role played by the valence electrons, studying condensed aromatic hydrocarbons, found an almost perfect agreement between the actual position of electrophilic attack and the site of large electron density. In the search for a quantitative correlation between reactivity and electronic configuration, the concept of frontier orbitals was established: for the case of reaction with an electrophilic reagent or electron acceptor, the position that is most susceptible to attack is that of the highest occupied (molecular) orbital (HOMO). For the case of reaction with a nucleophilic reagent or electron donor, the lowest unoccupied (molecular) orbital (LUMO) plays the principal role. When two molecules approach each other, the reaction will start with a nuclear configuration that favors best HOMO–LUMO overlap. Thus, reactivity indices of the frontier type identify sites in a molecule where new chemical bonds are likely to form.

Pearson [45] introduced the electronic "softness", the magnitude of the change in the electronic structure of a molecule due to a change of the number of electrons in the system, as a measure of reactivity. Species are then classified as "soft" if only a small energy is required to change their electronic configuration, i.e., if the valence electrons are easily distorted, polarized, removed, or added. A "hard" species has the opposite properties, holding its valence electrons more tightly [45,46]. The utility of these concepts is based on the so-called hard and soft–acid base (HSAB) principle formulated by Pearson [45] which states that when two reactants interact, either hard–hard or soft–soft interactions are preferred. In the case of poly-atomic or extended systems, the HSAB principle is used in a local version: the soft (hard) parts of one reactant prefer to interact with soft (hard) parts of the other. An example of a soft–soft interaction is CO adsorption on a metal surface. It involves electron donation from the molecule, which is considered to be the base, to the metal substrate which may be regarded as the acid; hence it can be called an acid–base reaction. Soft–soft interactions typically involve covalent-like bond formation and can be described as "frontier controlled" since the reactivity is essentially determined by the frontier orbitals. A hard–hard reaction occurs predominantly between highly charged species that are difficult to polarize or ionize, where the interaction is electrostatic in nature involving very little charge transfer. Interactions of this type are called "charge controlled". An example of a hard base (donor) is OH^- and a hard acid (acceptor) is, for example, Mg^{2+}. From these considerations the soft–soft and hard–hard interaction preference can be understood; e.g. soft bases will not be able to achieve a strong covalent bond with a hard acid which has a low tendency to accept electrons, nor can a strong electrostatic bonding be achieved due to the small or negligible charge of the soft base.

Parr and Yang [47] have expressed these ideas within DFT and defined the "local softness" in terms of the change in the electron density due to a change of the number of electrons of the system. Analogously, for metals, the local softness is expressed in terms of the response of the electron density to a change in the electron chemical potential. More precisely, it was shown that the local softness is the electron density of states at the Fermi level screened by a response function closely related to the static dielectric function [48]. It is intuitively clear that for both cases (semiconductors and metals) this is closely related to the HOMO and LUMO concept mentioned earlier.

For extended systems molecular orbitals and levels are not well defined and models of chemical reactions at surfaces were formulated using basis sets of localized atomic-like orbitals and the projected density of states (see e.g. Refs. [49–52]). Wilke et al. introduced the "local isoelectronic reactivity" [53], which is closely related to the local polarizability of valence electrons induced by an atom or molecule starting to chemically interact with the surface. The spatial variation of Wilke's function essentially gives the density of the LUMO (represented by regions of positive Wilke density) and HOMO (represented by regions of negative Wilke density) [53]. With similar limitations as those from which the general Fukui theory suffers, Wilke's representation gives a rationalization of the initial preference of a reaction pathway.

As already mentioned, chemical reactivity theory can give quantitative information only about the early stages of a chemical interaction, because in most cases the actual reaction will be determined by the non-linear response of the electron density to a local perturbation, and it will be governed by many states, not just the states at the Fermi energy. Despite this restriction, the local softness, in connection with the HSAB principle, has become an important predictive tool in analyzing reactions between molecules (see e.g. Ref. [54]).

3.2. At the transition state

For strong overlap between the HOMO and LUMO of reactants, the concept of reactivity indices breaks down. For dissociation and other reactions at metal surfaces we believe that this warning applies frequently, and the main reason for this difference between gas phase chemistry and the chemistry at metal surfaces is that in the interaction of a molecule with a surface, we are dealing with very unequal partners. The approaching molecule is able to translate and rotate, but the substrate is not (besides small relaxations of surface atoms). Furthermore, a metal substrate has a nearly infinite number of electrons, which implies that the position of the highest occupied and lowest unoccupied energy level is fixed. But for the molecule, the states can shift significantly, and if the highest occupied level is only fractionally filled, this level will not remain unchanged, but it will be subject to electron transfer and adjust to the substrate Fermi level. Also, it has been found from studies of the dissociation of H_2 at metal surfaces, through accurate first-principles calculations of high dimensional potential-energy surfaces (PESs), that the lowest energy barrier (when present) is actually very close to the surface and at a H–H distance which is significantly stretched (by about 100%) compared to the free molecule. Thus, the H–H bond is nearly broken when the molecule has reached the top of the energy barrier and the analysis showed that the differences between the behavior of H_2 at different metal surfaces should be described in a covalent picture. Earlier attempts, which applied a description in terms of Pauli repulsion, and/or frontier orbitals of the unperturbed non-interacting constituents do not account properly for the character and strength of the interaction. A more detailed discussion of these aspects is given in Ref. [4].

In Fig. 10 we summarize the view developed by Hammer et al. [52,55–57] in their analysis of H_2 at Cu(1 1 1) and H_2 at NiAl(1 1 0) (see also the earlier study by Hjelmberg and Lundqvist for H_2 at jellium [58]). At the transition state the interaction of the molecule with the surface has already produced a clear splitting into states which are bonding between the molecule and the substrate and ones which are antibonding. Assuming a substrate from the middle of the transition-metal series (e.g. Ru or Rh) implies that the low energy resonances, which are σ_g and σ_u derived, are filled with electrons. These states are bonding with respect to the molecule–substrate interaction, and thus their filling implies an attraction of the molecule to the surface. But the filling of the σ_u resonance also implies a weakening of the H–H bond. Thus, when the substrate Fermi level is in the middle of the d-band, we understand that molecules are strongly attracted to the surface and at the same time the molecular bond is broken. On the other hand, when the substrate Fermi level is well above the d-band, as for a noble metal, also the states which are antibonding with respect to the molecule–surface interaction become filled (the high energy DOS in panels (c) and (d) of Fig. 10). This implies that the net interaction between the molecule and the substrate is repulsive. This can be thought of as a so-called four-electron two-orbital interaction, in which the stabilization due to the occupied bonding orbital is weaker than the destabilization due to the occupation of the antibonding orbital. This is typically described as a consequence of Pauli repulsion (see e.g. Refs. [50,59]). Thus, an energy barrier is built up which hinders the dissociation.

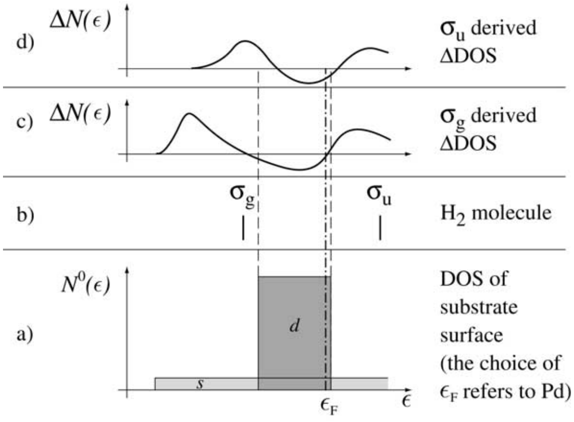

Fig. 10. Schematic description of the interaction of H_2 at the transition state toward dissociative adsorption at transition-metal surfaces. The bottom panel (a) shows the density of states for a transition metal before adsorption, and panel (b) shows the energy levels of a free H_2 molecule: the bonding state $[\phi_{\sigma_g} = \phi_{\mathrm{H1s}}(\mathbf{R}_1) + \phi_{\mathrm{H1s}}(\mathbf{R}_2)]$ and the antibonding state $[\phi_{\sigma_u} = \phi_{\mathrm{H1s}}(\mathbf{R}_1) - \phi_{\mathrm{H1s}}(\mathbf{R}_2)]$. The σ_g-level is filled with two electrons and the σ_u-level is empty. The interaction between the H_2 σ_g-level and the substrate s- and d-bands gives rise to a broadening and the formation of an antibonding level at about the upper edge of the d-band and a bonding level below the d-band—see panel (c). Panel (d) shows that the interaction between the H_2 σ_u-level with the substrate s- and d-bands gives rise to a broadening and the formation of a bonding level (at about the lower edge of the d-band) and an antibonding level (above the d-band). From Ref. [4].

Calculations for the dissociation of H_2 at Rh, Pd, and Ag surfaces (i.e. for substrates from the left to the right in the periodic table) found that for Rh most pathways are not hindered, for Pd most pathways are hindered, and for Ag there is always an energy barrier hindering the dissociated adsorption [60]. From Fig. 10 it is clear that and why Ag is chemically rather inert (its Fermi level is about 3 eV above the top of the d-band); but its left neighbor, Pd, is chemically more active. And the left neighbors of Pd, namely Rh and Ru, are even more so, because their Fermi levels are closer to the middle of the d-band. Of course, this trend is also seen in the cohesive energies, which is large for Ru and smoothly decreasing via Rh, Pd to Ag. It is the availability of occupied and unoccupied d-states which rules the chemical activity and bond strength. In the same spirit, Toulhoat [61], studying the strength of the nitrogen–metal bond in transition-metal nitrides as a function of the number of d-electrons, found that the bond strength decreases from the group VIA elements (configuration d^5s^1 or d^4s^2) with increasing number of valence electrons, being lowest for the noble metals (e.g. Cu), where the d-band is well below the Fermi level. He suggests that such ab initio derived bond lengths provide practical guides for research in catalysis design. Clearly, earlier work using the Andersen–Grimley–Newns Hamiltonian, or, equivalently, Nørskov's d-band center formulation, work on the same principle. In this context we also mention the early work of Pettifor on the development of our understanding of the nature of bonding of transition metals [62].

Obviously, the situation described by Fig. 10 falls outside the range of validity of the concepts discussed in Section 3.1, i.e., the position of the transition state and the subsequent dissociation are determined by strong covalent interactions. However, the general trend of the reactivity of various transition metal surfaces described above, is apparently also predicted by the reactivity indices. In the next subsection, we will see that in a full, dynamic description of H_2 dissociation as a measure of reactivity, a different conclusion will result. We will also see in Section 3.4 that an increased bond strength does not imply that the system is a good catalyst, but (besides other aspects) the bond strength should be intermediate.

3.3. The role of dynamics and statistics

To obtain a full description of surface reactivity, i.e. of the probability of dissociation, it is necessary to calculate the dynamics of the molecules approaching the surface. This subsection shows, that sometimes dynamical effects can be significant and differences from a theory that just considers reactivity indices, noticeable. A good quality theory of the dissociation dynamics was first developed by Gross et al. [6,9] and Kroes et al. [10], who took the high dimensionality of the PES into account and, studying H_2 dissociation, also treated the hydrogen nuclei as quantum particles. By comparison with a classical treatment of the dynamics, Gross and Scheffler [6] showed which quantum effects are important (mainly zero-point vibrations, and only little tunneling).

In Fig. 11 we display the sticking probability, S, for two different substrates, obtained by solving the Schrödinger equations for the nuclei. The sticking probability is the probability that an incoming H_2 molecule dissociates and that the atoms then adsorb at the surface. One could also say that $(1 - S)$ is the probability that an incoming H_2 molecule gets reflected back into the vacuum. One unexpected and surprising result of Fig. 11 is that for low kinetic energies ($E_i \lesssim 0.05$ eV) the sticking probabilities for the Pd and Rh substrates are very

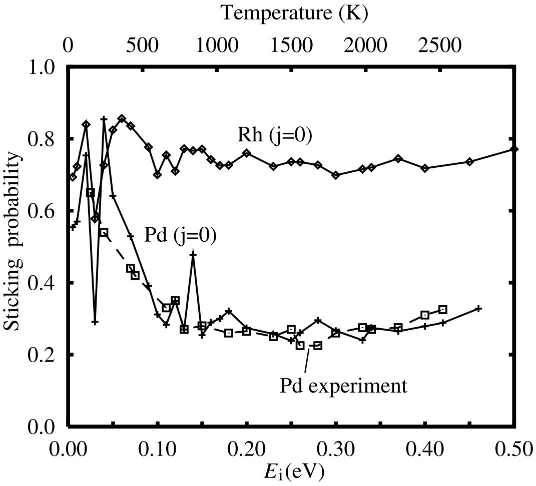

Fig. 11. Initial sticking probability (the probability that an incoming H_2 molecule dissociates and that the atoms adsorb at the surface) versus kinetic energy for an H_2 beam under normal incidence on a clean Rh(0 0 1) and Pd(0 0 1) surface. The H_2 molecules are in their rotational and vibrational ground state. Theoretical results are from Eichler et al. [60], and the experimental data are from Rendulic et al. [63]. We also mention that for H_2 at Ag(0 0 1) the calculations give a sticking probability of zero in the whole range of energies E_i shown in the figure.

similar. In view of the discussion of reactivity indices (Section 3.1) and the discussion of a strong covalent bond formation (Section 3.2), this is not understandable because at the Fermi level Rh has more occupied, and in particular, more empty d-states than Pd. Thus, Rh should be more reactive than Pd. Nevertheless, both substrates give a sticking probability as high as 75% for low temperature ($T \lesssim 250$ K). While for Rh the sticking probability always remains high, it decreases for Pd to about 25% when the temperature of the H_2 beam is increased. This is found in the theory as well as in the experimental data. The analysis of the H_2 dynamics revealed that the effect is best described by the word "steering", which means the same as on the road: If one is going slowly, one will make it well along a curvy street. However, when one is going too fast one is pulled out of the curve. Thus, molecules which are approaching slowly will be able to follow a pathway along curvy valleys of this high dimensional potential-energy landscape, and find the way toward the point where they can dissociate without an energy barrier. They will dissociate even if their initial orientation was unfavorable (e.g. perpendicular to the surface) because they are steered toward a more favorable transition-state geometry. On the other hand, fast molecules will not be able to make it around all the curves. They will bump against an energy barrier and be reflected back into the gas phase.

Thus, the behavior we see for the Pd substrate which increases the sticking to nearly 75% at low energies of the H_2 beam, is truly a dynamical effect. In a static picture the high reactivity of Pd cannot be understood. The efficiency of steering depends on the speed of the incoming molecule and on the shape of the PES. Therefore, to evaluate the sticking probability, which we consider a good measure of the surface reactivity, it is important to consider all degrees of freedom and the dynamics of the nuclei. In addition, it is necessary to include good statistics; a corresponding calculation for the results shown in Fig. 11, but calculated using molecular dynamics, would require more than 100,000 trajectories in order to obtain an adequate description. Obviously, as much as "steering" is important to understand the high reactivity of Pd at low E_i, for other systems, which on the grounds of the electronic-structure alone may be expected to exhibit a high reactivity, an "anti-steering" may occur, which drives approaching molecules not toward the best transition state, but against an energy barrier.

3.4. Weakening the adatom–surface bonds

In Sections 3.1–3.3 we dealt with "surface reactivity" in terms of the dissociation and/or adsorption of an approaching molecule. However, there is an additional aspect which determines whether or not a surface is possibly useful in a catalytic cycle: the adsorbed atom or molecule should not be bound too strongly, because otherwise there would be little or no reason for the next steps, namely diffusion on the surface in order to find a partner, and reaction toward an intermediate or the final reaction product. That is, a good catalyst is one that can efficiently dissociate molecules but not bind the adsorbates too strongly. In this section we will discuss two examples which highlight this point and show the importance of adsorbate–surface bonds being sufficiently weak, and how this can be achieved. Both examples refer to oxygen at ruthenium, with some reference to the CO oxidation.

From the above sections, one may expect that Ru, being situated in the middle of the transition-metal series, will exhibit a good reactivity. However, in standard UHV experiments its activity towards CO oxidation is very low [64]. This is because although Ru effectively dissociates molecular oxygen, it binds the oxygen atoms too strongly under these conditions [16,65]. In what follows we will see how this scenario can be improved.

In standard UHV experiments and exposing a Ru(0001) surface to O_2, the saturation coverage has been reported to be approximately half a monolayer [66,67]. Recent studies employing NO_2 or very high O_2 exposures have shown, however, that Ru(0001) can support higher coverages, for example, ordered structures with $\Theta = 0.75$ [68–70] and with $\Theta = 1$ [71], as had initially been predicted by DFT–GGA calculations [72].

Furthermore it was predicted that subsurface adsorption is possible but will occur only after completion of the monolayer structure at elevated temperatures ($T \approx 600$ K) [39,72–75]. Thus, the (apparent) oxygen saturation coverage noted above for low (or room) temperature UHV conditions and typical exposure by O_2, is solely due to kinetic hindering of the O_2 dissociation. This is part of the "pressure gap" problem, but as shown by Stampfl and Scheffler [72], if the reason is understood, it is possible to bridge the pressure gap.

In Fig. 12 it can be seen that the adsorption energy of oxygen at Ru(0 0 0 1) markedly decreases when the coverage increases. The reason can be well understood in terms of the repulsive interaction between the partially ionized O adatoms. For low coverage the adsorption energy is high and oxygen is satisfying its bonding needs well. Thus, this oxygen will not be keen on undergoing another chemical reaction (leading to the mentioned low CO_2 turnover rates in UHV [64]). The rationalization behind this statement is that energy barriers for diffusion and chemical reactions roughly scale with the energy of the initial state. Thus, even if a well bound initial state is less favorable than the end product of a surface chemical reaction, the energy barrier to reach the product is probably high. In relation to this, Alavi et al. [76] proposed on the basis of first-principles calculations, that the weakening of the O–Pt bond is a significant contribution to the energy activation barrier for CO_2 formation over the Pt(1 1 1) surface. Similar calculations were performed by Eichler and Hafner [77], where in addition, reaction of CO with molecular oxygen was investigated. We also note that in Fig. 9 calculated and measured TPD spectra for the O/Ru adsorbate system were shown, and one sees that oxygen from the high-coverage phase (i.e., where it is more weakly bound) leaves the surface at significantly lower temperature ($T \approx$ 900 K) than the oxygen from the low-coverage phase ($T \approx 1300$ K). In the 1 ML phase, the oxygen binding to the surface is still, however, sufficiently strong to disfavor a reaction with a CO molecule as indicated by DFT calculations [65].

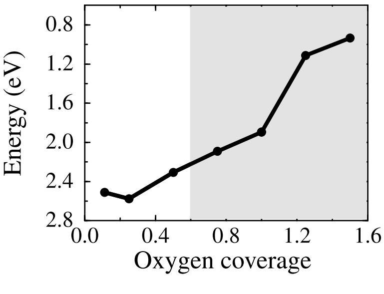

Fig. 12. Average adsorption energy of oxygen on Ru(0 0 0 1) for various coverages, with respect to 1/2 O_2. The coverage range $\Theta > 0.6$ is marked in gray to indicate that here O_2 dissociation is kinetically hindered. For coverages $\Theta > 1$ oxygen atoms also occupy subsurface sites [75] and a significant decrease in the average adsorption energy can be noticed.

From Fig. 12 it can be seen that for structures involving both on-surface and subsurface oxygen, the average bond strength is even weaker than for on-surface O alone. In view of this, the high-coverage phases of O/Ru(0 0 0 1) should be substantially more active towards CO oxidation than the lower coverage UHV phases. This is indeed the case as found by experiments performed using high O_2 gas pressures [78]. Adding to this, experimental work of Böttcher and Niehus [74], in agreement with recent calculations [75,79], pointed out that at high oxygen pressure Ru can accomodate much more than a monolayer (cf. Fig. 12). In fact, Böttcher et al. report an uptake corresponding to more than 30 ML and that this "loading" of the Ru with oxygen gives rise to a significant structural destabilization and the formation of oxide crystallites at the surface, which were shown to be RuO_2 [19]. This surface phase transition is nothing else than the dry corrosion mentioned in Section 1.3, and we see here an example where catalysis and corrosion meet: Böttcher et al. [18,80] and Over et al. [19] emphasize that the true catalyst, which is operative when the high activity of Ru for oxidation catalysis is discussed, is not the originally introduced Ru metal (which binds O too strongly) but the material which comes into being when Ru metal is in an oxygen atmosphere at high pressure and high temperature; that is, the predominant catalytic activity arises due to the presence of RuO_2. We will come back to this point in Section 4.

Our second example highlighting the importance of weak oxygen–ruthenium bonds for increased catalytic activity, addresses the recent work of Bonn et al. [81]. Here, the weakening of the bonds is induced by laser-light excitation. The laser light is mainly absorbed in the substrate, where it gives rise to a high density of hot electrons ($T_{\rm el} \approx 6000$ K). With a time delay, corresponding to some atomic vibrations (about 1–2 ps), the electron and phonon temperatures equilibrate, and then the temperature of both, phonons and electrons, is about 2000 K. Using 110 fs short laser pulses ($\hbar\omega = 1.5$ eV), Bonn et al. could show that CO_2 formation is enhanced during the initial time period, i.e., when the electrons are hot, but atomic vibrations not yet significant. Thus, electronic excitation enhances the desired reaction, a phenomenon known as photochemistry of a surface chemical reaction. With a noticeable time delay, CO was found to desorb. Obviously, this is a thermal desorption process, i.e. driven by the atomic vibrations. DFT calculations, evaluating the electron free energy, explained that the photochemistry of the CO_2 formation is largely driven by a weakening of the O–Ru bond, i.e., for high electron temperatures the oxygen binding energy is significantly reduced (see Fig. 13). This is due to the presence of an O–Ru antibonding state just above the Fermi energy (see the shaded part of the density of states in Fig. 13). Hence we see that weakening of the strong O–Ru bond can either be realized by modifying the catalyst's surface structure, in our example by increasing the O concentration, or by externally stimulating the chemical reaction. In relation to the latter, recently it was demonstrated using (third generation) synchrotron radiation, that site-selective targeting and breaking of individual bonds, even for identical atoms which are only in slightly different chemical environments could be achieved [82].

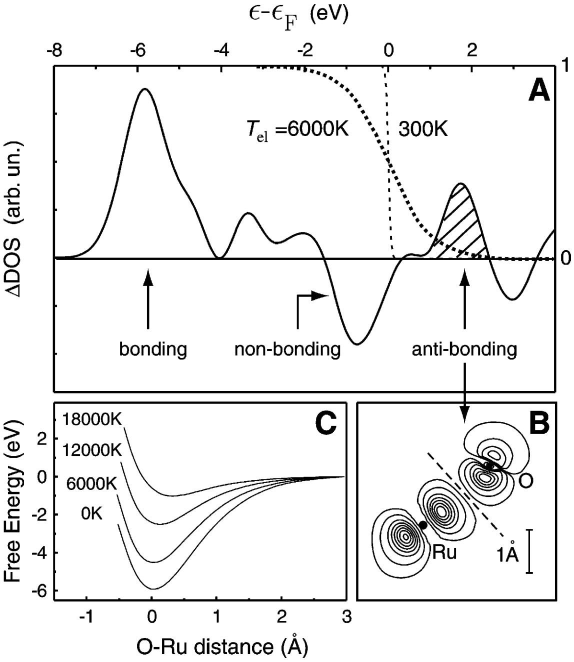

Fig. 13. Results of DFT–GGA calculations for (2 × 1)-O on Ru (0001). (A) The change in the density of states (ΔDOS) upon adsorption. A bonding state appears well below the Fermi level and an antibonding state at 1.7 eV above. The Fermi functions $f(T_{\rm el}, \epsilon - \epsilon_{\rm F})$ at $T_{\rm el} = 300$ and 6000 K (referred to the right ordinate axis) demonstrate that with increasing temperature the antibonding level becomes populated. (B) Electron density of the antibonding state at $\epsilon_{\rm F} + 1.7$ eV. (C) Free energy as a function of O–Ru distance and electronic temperature. The bond is strongly weakened as the electron temperature increases (after Ref. [81]).

The importance of an optimum bond strength was further illustrated in recent studies by Toulhoat et al. [83] and Raybaud et al. [84]. Here the hydrodesulfurization process was considered, for which transition-metal sulfides (TMS) are the only class of materials that act as good catalysts (crude oil contains many organosulfur compounds and one wants to abstract the sulfur, producing H_2S and hydrocarbons). Toulhoat et al. showed that if the TM–S bond strength (i.e. here, the cohesive energy per metal–sulfur bond) is calculated from first-principles, one observes the so-called "volcano" curve [14,85], i.e., it exhibits a maximum in reactivity for an intermediate bond strength (here for ruthenium sulfide), or other measure of the stability of the reaction intermediate. In relation to this, Raybaud et al., studying in particular MoS_2, showed how such an optimum bond strength and increased activity could also be achieved through an appropriate mixture of selected atomic species to the TMS. The typical volcano-shaped curves were first proposed by Balandin [85]. They reflect the Sabatier principle which emphasized the intermediate compound, in that it must be stable enough to form, but not too stable since it must decompose to yield the final product. This concept, as put forward by catalytic chemists, has long been a guiding principle in efforts to develop or improve catalysts. Now, with state-of-the-art first-principles calculations at our finger-tips, we can directly use and explore these early principles, which may well provide exciting new possibilities in the near future.

4. The full concert

In the previous sections we described the state-of-the-art of electronic-structure theory for surfaces and adsorption, dissociation dynamics and statistics, and thermodynamics of surface phase transitions. Special attention was given to the influence of temperature and pressure. The various aspects discussed will all play a role in modeling and understanding a sustained catalytic reaction, or the time and structural evolution of the growth of a corrosion film on a metal surface. The new aspect in this sentence, which will be emphasized in the present section, is in the words "sustained" and "evolution", and this implies the necessity to describe time scales of the order of milliseconds or more, and length scales of 10 nm or more. Thus, an adequate theory of catalysis and corrosion should describe the atomistic level, i.e. a time period of a few femtoseconds, the formation of small islands (microseconds), as well as the evolution of mesoscopic and macroscopic structures (tenths of seconds). In Table 1 we list different theoretical approaches which address different time and length scales. These techniques should be regarded as complementary to each other rather than as alternatives, and possibly they should be combined. We will discuss the latter in this section.

Previous and present "academic" research is mainly concerned with isolated molecular processes. While this is indeed important, we also note that it is not sufficient for a realistic modeling and trustworthy understanding of catalysis or the evolution of a corrosion film. In addition to the knowledge of possibly relevant, individual molecular processes, it is in fact crucial to know if they can, and how they will, "play together". Let us make this point more clear, again through the example of the oxidation of carbon monoxide at Ru(0 0 0 1). At high gas pressures and temperatures, a Ru surface will at some stage start to transform into an oxide. Hence, the CO oxidation reaction could either take place on patches of this newly formed oxide, or occur on those parts of the surface that are still unchanged. The surface-science approach to this problem was hitherto to focus on perfect surfaces of one or the other. However, the crucial point for catalysis, is to understand how, and how often, reaction to CO_2 is actually realized; and after reaction and desorption events have taken place, how, and how fast they are built up again. Thus while it is useful, and even necessary, to study the mentioned isolated surface reactions, whether or not they ultimately play a significant role in "the full concert" of various molecular processes, that must play together in a sustained catalytic reaction, remains to be seen. We note in passing that the processes of CO oxidation have been studied experimentally as well as by DFT calculations but we only refer here

Table 1
The time and length scales handled by different theoretical approaches to study chemical reactions, the evolution of new structures, and crystal growth

	Type of information	Time scale	Length scale
DFT	Microscopic	–	$\lesssim 10^3$ atoms
Ab initio molecular dynamics	Microscopic	$t \lesssim 100$ ps	$\lesssim 10^2$ atoms
Semi-empirical molecular dynamics	Microscopic	$t \lesssim 10$ ns	$\lesssim 10^3$ atoms
kMC	Microscopic to mesoscopic	1 ps $\lesssim t \lesssim$ 1 h	$\lesssim$ 1 μm
Rate equations	Averaged	0.1 s $\lesssim t \lesssim \infty$	All
Continuum equations	Macroscopic	1 s $\lesssim t \lesssim \infty$	$\gtrsim$ 10 nm

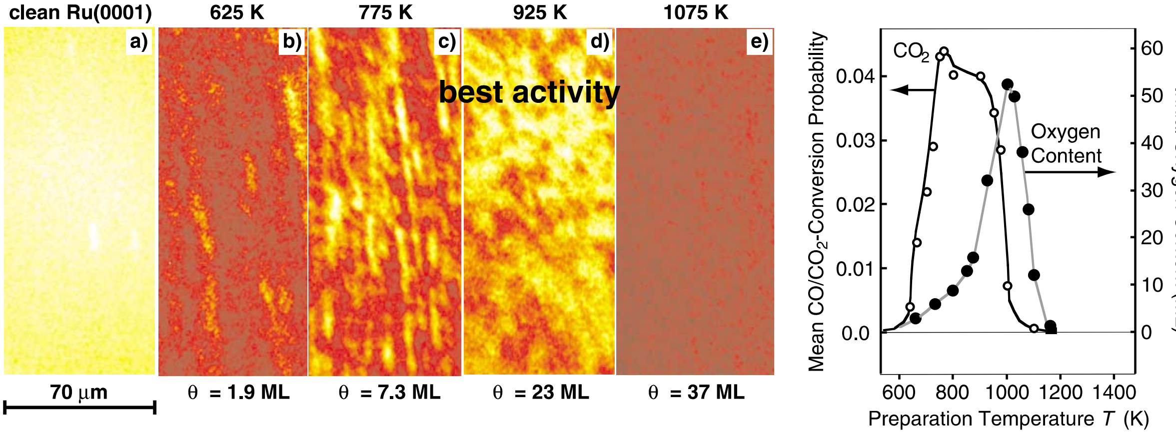

Fig. 14. Oxidation of Ru(0 0 0 1) and corresponding CO → CO_2 formation rate. Left: PEEM images of the Ru(0 0 0 1) surface, when clean and when exposed to an O_2 atmosphere of 1 mbar for 1 s at different temperatures (noted at the top of the figure). The resulting uptake of oxygen by Ru (noted at the bottom of the figure) was determined by temperature programmed desorption (see Ref. [20] for details). Regions with different shades correspond to materials with different workfunctions, Φ: White regions (highest photoelectron energy) have $\Phi = 5.3$ eV, and black regions (no photoelectron emission) have $\Phi > 6$ eV. Right: Rate of CO_2 formation over the differently prepared Ru + O systems.

to the book chapter by Scheffler and Stampfl [4] and a recent publication by Kim et al. [86] for details.

In Fig. 14 we show recent photoemission electron microscopy (PEEM), temperature programmed desorption, and surface reactivity experiments for the CO oxidation reaction over Ru surfaces prepared with different and systematically controlled concentrations of oxygen in the surface region [20]. These results demonstrate that depending on the pressure and temperature, different phases coexist on the surface and this coexistence apparently markedly affects the reactivity. The highest reactivity was found for conditions where a significant amount of O is stored on and in the surface, and where quite differently behaving materials (cf. the bright and dark domains in Fig. 14) coexist on a mesoscopic scale. We note that although Ru behaves quite differently to other transition metals (see Ref. [4] for details), the important issue, likely to be relevant to all realistic catalytic processes, is that *complexity* plays a more significant role than typically assumed—correspondingly, this aspect must also apply to theoretical descriptions. In this respect we envisage that for relatively "simple" catalytic reactions such as CO oxidation over transition metals, understanding and a good quality theoretical treatment will be achieved soon, e.g. in less than 10 years. In what follows we will explain what we believe should be the next steps in modeling and achieving understanding of catalysis. Analogously the modeling of corrosion may proceed.

Surface science, catalysis research, and the science of crystal growth (which includes the kinetics of formation of the corrosion compound) have to undergo (and are already undergoing) a noticeable change. Present day methods to develop new catalysts or to improve materials properties are still mainly done by trial and error. And the theoretical modeling of technologically relevant chemical processes so far proceeds by employing phenomenological methods (e.g. rate equations or hydrodynamic theories) together with effective parameters. Typically the latter have a very limited physical meaning and are not transferable, e.g. to situations with significantly different temperature, pressure, or material composition. This may be called "modeling without microscopic understanding". Using this term does not imply that it is bad or not useful. In fact, so far it has been very useful, but now there is clearly a need for improvement. In particular for basic research, it is clear that the next step, i.e. the development of a theoretical approach "with microscopic understanding", is what should be done now. We note in passing that combinatorial chemistry, appreciating the importance of complexity, attempts to improve the efficiency of the trial and error approach. This seemingly implies that microscopic understanding is no longer relevant, but this impression is in fact incorrect. In order to create a meaningful catalog of 10,000 or more experiments, i.e. for constructing a meaningful "descriptor" for the various studied systems and conditions so that directed searches (rather than blind scans) can be carried out, microscopic understanding is indeed necessary.

In the history of surface science we have worked our way down many orders of magnitude (both experimentally and theoretically) from the rate equations of the beginning of this century to the microscopic description of individual elementary processes, and have gained much understanding. Now, in the new century, we can begin to work our way back up, introducing some controlled complexity with a microscopic basis, and attempting to assemble these processes in a unified theoretical description of, for example, a sustained catalytic reaction or the evolution or a corroding surface. One promising approach that we see to do this is outlined below.

A single molecular process can be studied either by performing a molecular dynamics simulation or by using transition-state theory. Both approaches typically will give the same result. Problems with the latter may occur when the energy barrier is comparable to the thermal energy and correlated effects cannot be neglected. With respect to the former, presently (and the next years) due to computer limitations, it is unlikely that it will be possible to perform MD calculations with good statistics for surface reactions, that is, for the "whole concert" of reactions involved in describing surface phenomena. Thus, typically transition-state theory is the preferred approach (calculating energy barriers and prefactors by DFT). When there are competing processes (and typically there are), a statistical sampling becomes crucial. Handling of the statistics is the essence of the kMC method [13]. It describes the time evolution of chemical reactions and/or growth in terms of "the typical dynamics", treating the occurrence of the various events statistically as well as the progression of time. Consequently it is the most efficient approach to study long time (e.g. seconds or even minutes) and large length scales (e.g. surface areas of 10^4 nm^2) but still able to provide atomistic information. Up until recently kMC was only used for very simplified model systems, e.g. treating surfaces as simple-cubic lattices, employing empirical parameters, and, when a compound was modeled, the two different species were often treated as one single "effective" species. In this way modeling was possible by using very few parameters. In fact, because the possible microscopic processes and the associated energy barriers were unknown (and this situation still holds for many systems), there was no way to do it differently.

The key idea in kMC is that the microscopic processes are described by rates. Thus, the first step is the analysis and identification of all possibly relevant processes and determination of the associated rate. Once the rates are known, the various processes and their interplay can be handled by standard methods from statistical physics. The two basic quantities describing the rate of a process $\Gamma = \Gamma_0 \exp(-\Delta E/k_\mathrm{B}T)$, are the attempt frequency Γ_0 and the difference ΔE, of the total energy with the particle at the minimum and at the saddle point of the potential energy curve along a reaction path of the process. T is the temperature and k_B the Boltzmann constant. A typical kMC cycle consists of, (i) from inspection of all atoms of the system, determine the atomic processes that are possible and calculate the rates, (ii) generate two random numbers, (iii) advance the system (i.e. move an atom) according to the atom and process selected by the first random number, (iv) increment the clock according to the rates and the second random number.

Ruggerone et al. [87] and Ratsch et al. [88] were the first to employ energy barriers calculated by DFT in the kMC approach for studying nucleation and growth. In a subsequent study, also prefactors were calculated by DFT [89]. For compounds, where the interplay of surface reconstruction, diffusion, dissociation, and two chemically different species also play a role, the description becomes more complicated as evident in the recent ab initio kMC study of Kratzer and Scheffler [90,91]. This study describes the deposition of $As_2 + Ga$ on a reconstructed GaAs surface in order to study the temperature and pressure dependence of diffusion, dissociation, island nucleation, and growth. The treatment of catalysis could proceed analogously, but in view of the above mentioned mesoscopically structured surface, which contains different materials of very different properties, the corresponding modeling will be even more involved. In this context we also note the recent work by Hansen and Neurock [92] who performed Monte Carlo calculations based on a mixed scheme of first-principles calculations and semi-empirical models, to study nitric oxide decomposition on Rh(1 0 0) and ethylene hydrogenation over Pd(1 0 0). The work by Kratzer and Scheffler [90,91] showed that "modeling with microscopic understanding" requires taking into account more than 30 processes. This is a significantly higher number than that used for semi-empirical studies where one gets along with about five "effective" processes. Still, the risk that a relevant process may be overlooked in a DFT–kMC calculation certainly exists. For example, Ovesson et al. [93] recently showed that diffusion rates at island corners are noticeably different to what was assumed in the earlier work [87,88], and this had important consequences for the island shapes, that develop under growth conditions. The description and inclusion of all relevant and important processes is one of the challenges that will have to be faced in order to perform and elaborate upon such a description.

Over the last decades, years, and months much has been learned about the chemistry at surfaces, which is often noticeably different to the chemistry between gas phase molecules: Gas phase chemistry is well established, but surface-science chemistry is still in a very early stage and full of surprises. We illustrated this through two examples that revealed that wide-held expectations and understanding were incorrect, namely, that it is not the Ru metal which is the main catalyst for CO oxidation at high pressure and temperature, nor is it the metal oxide Fe_2O_3 that is the main catalyst for styrene production under industrial conditions, but it is a new material which is produced during the induction period. And it is the environment that controls composition and structure, and the detailed material composition seems to be essential. With this in mind, we may even speculate that also for other oxidation catalysts the initially introduced metal does not just adsorb oxygen, but the catalytically active material contains subsurface oxygen as well as surface-oxide phases, some of them may even be unknown to date, as they may not exist under UHV conditions. From the theoretical side, we see the need for more accurate electronic-structure calculations (as well as molecular dynamics) for surface processes, but the big next step will be the combining of electronic-structure theory with dynamics and statistical mechanics of catalysis and corrosion on realistic time and length scales, at realistic temperatures and pressures. We have described how we believe this goal can be achieved, but also note that many difficulties are to be expected when this is really formulated and programmed. However, we are convinced that the knowledge gained along the way will be significant and consequential.

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