Catalysis and Electrocatalysis at Nanoparticle Surfaces



edited by Andrzej Wieckowski Elena R. Savinova Constantinos G. Vayenas

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Foreword

Catalysis and Electrocatalysis at Nanoparticle Surfaces reflects many of the new developments of catalysis, surface science, and electrochemistry. The first three chapters indicate the sophistication of the theory in simulating catalytic processes that occur at the solid–liquid and solid–gas interface in the presence of external potential. The first chapter, by Koper and colleagues, discusses the theory of modeling of catalytic and electrocatalytic reactions. This is followed by studies of simulations of reaction kinetics on nanometer-sized supported catalytic particles by Zhdanov and Kasemo. The final theoretical chapter, by Pacchioni and Illas, deals with the electronic structure and chemisorption properties of supported metal clusters.

Chapter 4, by Batzill and his coworkers, describes modern surface characterization techniques that include photoelectron diffraction and ion scattering as well as scanning probe microscopies. The chapter by Hayden discusses model hydrogen fuel cell electrocatalysts, and the chapter by Ertl and Schuster addresses the electrochemical nanostructuring of surfaces. Henry discusses adsorption and reactions on supported model catalysts, and Goodman and Santra describe sizedependent electronic structure and catalytic properties of metal clusters supported on ultra-thin oxide films. In Chapter 9, Marković and his coworkers discuss modern physical and electrochemical characterization of bimetallic nanoparticle electrocatalysts.

Bönnemann and Richards lead off the section on synthetic approaches with a discussion of nanomaterials as electrocatalysts to tailor structure and interfacial properties. Teranishi and Toshima as well as Simonov and Likholobov discuss preparation and characterization of supported monometallic and bimetallic nanoparticles.

Van der Klink and Tong cover NMR studies of heterogeneous and electrochemical catalysts, and X-ray absorption spectroscopy studies are the focus of the chapter by Mukerjee. In Chapter 15, Stimming and Collins discuss STM and infrared spectroscopy in studies of fuel cell model catalyst.

Lambert reviews the role of alkali additives on metal films and nanoparticles in electrochemical and chemical behavior modifications. Metal-support interactions is the subject of the chapter by Arico and coauthors for applications in low temperature fuel cell electrocatalysts, and Haruta and Tsubota look at the structure and size effect of supported noble metal catalysts in low temperature CO oxidation. Promotion of catalytic activity and the importance of spillover are discussed by Vayenas and coworkers in a very interesting chapter, followed by Verykios's examination of support effects and catalytic performance of nanoparticles. In situ infrared spectroscopy studies of platinum group metals at the electrocatalysts for fuel cells, and Coq and Figueras address the question of particle size and support effects on catalytic properties of metallic and bimetallic catalysts.

In Chapter 24, Duo and coworkers discuss metal oxide nanoparticle reactivity on synthetic boron–doped diamond surfaces. Lamy and Léger treat electrocatalysis with electron-conducting polymers in the presence of noble metal nanoparticles, and new nanostructure materials for electrocatalysis are the subject of the final chapter, by Alonso-Vante.

There is no doubt that this book will be a valuable addition to the library of surface scientists, electrochemists, and those working in interface sciences who are interested in research that is being carried out at the frontiers of solid–liquid and solid–gas interfaces as well as nanomaterials. The contributors are outstanding senior researchers and the volume gives a glimpse of the present and the future in this frontier area of physical chemistry and interface chemistry: molecular-level catalysis and electrochemistry, and their applications in the presence of nanoparticles. The editors should be commended for doing such an excellent job in collecting superb chapters for this outstanding volume.

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Preface

Catalysis and Electrocatalysis at Nanoparticle Surfaces is a modern, authoritative treatise that provides comprehensive coverage of recent advances in nanoscale catalytic and electrocatalytic reactivity. It is a new reference on catalytic and electrochemical nanotechnology, surface science, and theoretical modeling at the graduate level.

Heterogeneous catalysis and aqueous or solid-state electrochemistry have been treated traditionally as different branches of physical chemistry, yet similar concepts are used in these fields and, over the past three decades, similar surface science techniques and ab initio quantum mechanical approaches have been used to investigate their fundamental aspects at the molecular level. The growing technological interest in fuel cells-both high-temperature solid oxide fuel cells (SOFC) and low-temperature polymer electrolyte membrane (PEM) fuel cells-has drawn the attention of the electrochemical community to three-dimensional electrodes with finely dispersed active components (metals, alloys, semiconductors) anchored to appropriate conducting supports. This has raised the question of specific electrochemical properties of small-dimension systems. Utilization of nano-sized materials introduces a number of phenomena specific for nanoscale, including particle size effects, metal-support interactions, and spillover, which are common for heterogeneous catalysis and electrocatalysis, and calls for joint efforts from the experts in these fields. This has brought the catalytic and electrochemical communities closer, as the need for heterogeneous catalytic knowledge in designing and operating efficient fuel cell anodes and cathodes is being more widely recognized. The electrical potential dependence of the electrochemical (electrocatalytic, i.e., net charge transfer) reaction rate has traditionally been considered a characteristic feature that distinguished it from the catalytic (no net charge transfer) reaction rate. Yet recent advances have shown that this distinction is not so rigid, as the rates of catalytic processes at nanoparticles in contact with solid or aqueous electrolytes also depend profoundly on catalyst potential, similar to the electrochemical reaction rate, and that a classic electrochemical double-layer approach is also applicable to the kinetics of catalytic reactions.

The collection of 26 invited chapters by prominent scholars originating from both the electrochemical and the catalytic schools of thought portrays this growing and mutually enriching merge of the fields of heterogeneous catalysis and electrocatalysis to address new technological and fundamental challenges of catalytic and electrocatalytic reactivity at nanoparticle surfaces.

Comprehensiveness is the key qualifier for this book. Its unique feature is that it provides nearly complete coverage of the main topics in contemporary nanoscale catalysis and electrocatalysis, with coherent, state-of-the-art presentation of theory, experimentation, and applications. This is the first volume of its kind to bring together such a broad and diverse profile of surface science and electrochemistry from the perspective of unique nanoscale surface properties. Similarly, it emphasizes the emergence and progress of knowledge of nanoparticle surface properties, the newest subfield of surface science and electrochemistry, which has not been reviewed before except in selected proceedings volumes. Surface science and electrochemical surface science, jointly presented in this volume, have enabled scientists to develop atomic- and molecular-level perspectives of reactions occurring at gas–solid and liquid–solid interfaces. Such perspectives, both current and forecast for the future, are amply demonstrated.

The strength of the field lies in its employment of basic science for technological applications, in relation to materials, catalysis, and energy efforts. The main thrust of this book is that it presents and unifies two main interfaces for use in heterogeneous catalysis and electrocatalysis, for both basic science and applications. The contributors were asked to make their chapters accessible to advanced graduate students in surface science, catalysis, electrochemistry, and related areas. The tutorial feature of the volume adds to its strength and educational value.

The book is divided into six parts: theory of nanoparticle catalysis and electrocatalysis; model systems from single crystals to nanoparticles; synthetic approaches in nanoparticle catalysis and electrocatalysis; advanced experimental concepts; particle size, support, and promotional effects; and advanced electrocatalytic materials. This facilitates access to the general reader's interests. Each chapter begins with a summary and a table of contents to provide an overview of its scope.

Part I presents the state of the art of the theory of catalysis and electrocatalysis at clusters and nanoparticles. This section provides the current frame of modeling of the interaction of clusters with substrates as well as catalytic and electrocatalytic kinetics on clusters and nanoparticles, including ab initio quantum mechanical calculations, and epitomizes recent advances in understanding the relation between electronic structure and catalytic/electrocatalytic activity.

Part II addresses the key question of how electronic and geometric properties of catalytic surfaces change upon moving from single crystals to nanoparticles and how this influences their catalytic/electrocatalytic activity. The use of model catalysts and electrocatalysts in conjunction with powerful surface spectroscopic techniques provides new insight into the unique phenomena observed upon decreasing the size of catalyst particles down to nanoscale and builds a link between catalysis and electrocatalysis at perfect single crystals and nanoparticles. The chapters in this section scrutinize approaches to electrochemical nanostructuring of surfaces and provide insight into unique behavior of small, confined systems.

Preface

Part III presents the state of the art of the synthesis of nanoparticle catalysts and electrocatalysts, including bimetallic nanoparticles. Particular emphasis is given to carbon-supported nanoparticles due to their technological significance in the fabrication of electrodes for PEM fuel cells.

Part IV describes recent breakthroughs in the use of advanced experimental techniques for the in situ study of nanoparticle catalysts and electrocatalysts, including X-ray absorption spectroscopy, NMR, and STM.

Part V addresses the critical issues of particle size effects, alloying, spillover, classic and electrochemical promotion, and metal–support interactions on the catalytic and electrocatalytic performance of nanoparticles. Recent experimental evidence is presented on the functional similarities and operational differences of promotion, electrochemical promotion, and metal–support interactions.

Part VI discusses novel advanced electrocatalytic materials, including polymerembedded nanoparticle electrodes for PEM fuel cells and synthetic diamond– supported electrocatalyst nanoparticles for toxic organic compound treatment.

This book will be an indispensable source of knowledge in laboratories or research centers that specialize in fundamental and practical aspects of heterogeneous catalysis, electrochemistry, and fuel cells. Its unique presentation of the key basic research on such topics in a rich interdisciplinary context will facilitate the researcher's task of improving catalytic materials, in particular for fuel cell applications, based on scientific logic rather than expensive Edisonian trial-anderror methods. The highlight of the volume is the rich and comprehensive coverage of experimental and theoretical aspects of nanoscale surface science and electrochemistry. We hope that readers will benefit from its numerous ready-to-use theoretical formalisms and experimental protocols of general scientific value and utility.

> Andrzej Wieckowski Elena R. Savinova Constantinos G. Vayenas



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Theory and Modeling of Catalytic and Electrocatalytic Reactions

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CHAPTER CONTENTS

- 1.1 Introduction
- 1.2 Overview of Computational Methods
- 1.3 Reactivity and Catalyst Electronic Structure
- 1.4 The Solvent in Electrode Reactions
- 1.5 Monte Carlo Simulations of Catalytic Reactions
- 1.6 Conclusions

SUMMARY

A brief overview is given of the main theoretical principles and computer modeling techniques to describe catalytic and electrocatalytic reactions. Our guiding principles in understanding the relationship between electronic structure and catalyst performance are the periodic table and the Sabatier principle. We discuss the different modeling tactics in describing quantum-mechanically adsorbate-surface interactions (i.e., cluster vs. slab models) and their accuracy in modeling (small) catalyst particles. The role of the solvent in electrocatalytic processes is described both from the point of view of quantum-chemical density-functional theory calculations, and from more classical Marcus theory-type considerations using molecular dynamics simulations. Furthermore, we discuss how kinetic Monte Carlo

methods can be used to bridge the gap between microscopic reaction models and the catalyst's macroscopic performance in an accurate statistical and mechanical way.

1.1 INTRODUCTION

With the incessant boom in computational power of present-day computers, the role of theory and modeling in the understanding and development of catalytic processes is becoming increasingly important. Theory and computational modeling have already played a significant role in heterogeneous gas-phase catalysis for quite some years, but comparable developments in the electrocatalysis of reactions at metalliquid interfaces have been less forthcoming. However, new theory developments in electrochemistry, the emergence of new computational possibilities with modern machines and codes, as well as the increasing overlap between electrochemistry and surface science promise a similarly prominent role of "computational electrochemistry" in the electrocatalysis community.

The aim of this chapter is to provide the reader with an overview of the potential of modern computational chemistry in studying catalytic and electrocatalytic reactions. This will take us from state-of-the-art electronic structure calculations of metal-adsorbate interactions, through (ab initio) molecular dynamics simulations of solvent effects in electrode reactions, to lattice-gas-based Monte Carlo simulations of surface reactions taking place on catalyst surfaces. Rather than extensively discussing all the different types of studies that have been carried out, we focus on what we believe to be a few representative examples. We also point out the more general "theory" principles to be drawn from these studies, as well as refer to some of the relevant experimental literature that supports these conclusions. Examples are primarily taken from our own work; other recent review papers, mainly focused on gas-phase catalysis, can be found in [1–3].

The next section gives a brief overview of the main computational techniques currently applied to catalytic problems. These techniques include ab initio electronic structure calculations, (ab initio) molecular dynamics, and Monte Carlo methods. The next three sections are devoted to particular applications of these techniques to catalytic and electrocatalytic issues. We focus on the interaction of CO and hydrogen with metal and alloy surfaces, both from quantum-chemical and statisticalmechanical points of view, as these processes play an important role in fuel-cell catalysis. We also demonstrate the role of the solvent in electrocatalytic bondbreaking reactions, using molecular dynamics simulations as well as extensive electronic structure and ab initio molecular dynamics calculations. Monte Carlo simulations illustrate the importance of lateral interactions, mixing, and surface diffusion in obtaining a correct kinetic description of catalytic processes. Finally, we summarize the main conclusions and give an outlook of the role of computational chemistry in catalysis and electrocatalysis.

1.2 OVERVIEW OF COMPUTATIONAL METHODS

1.2.1 Electronic Structure Calculations

Electronic structure calculations are generally concerned with solving the electronic ground state of a certain molecular ensemble based on first-principles quantum mechanics. The techniques are called *ab initio* if they require only the atomic numbers of atoms involved in the ensemble, and no adjustable parameters taken from experiment or other calculations. A good introduction into the various ab initio and other quantum-chemical methods is given in Jensen's book [4].

By far the most popular method currently used in the quantum-chemical modeling of adsorbate–substrate interactions is that based on the density functional theory (DFT). Contrary to the more "classical" quantum-chemical techniques, DFT is not directly based on electronic wave functions but rather on electronic density. The formal cornerstone of DFT is a theorem derived by Hohenberg and Kohn [5], which states that the ground-state electronic energy is a unique functional of the electronic density n(r), with r the space coordinate. In other words, there exists a one-to-one correspondence between the r-dependent electronic density of the system and the energy. However, the exact functional giving the exact energy is not known, and in practice one must therefore resort to one of the many approximate expressions available. The quality of these functionals is now such that one may calculate overall energies to within an accuracy of about 5–10% of the exact result. For many purposes, this accuracy is quite sufficient.

In practical calculations, the electronic density is still calculated from wave functions, using a method originally devised by Kohn and Sham [6]. These so-called Kohn–Sham orbitals correspond to a "virtual" system of noninteracting electrons, similar to Hartree–Fock methods. Even though these Kohn–Sham orbitals have no clear physical meaning, they may still be quite useful in interpreting the results from a DFT calculation in terms of molecular orbital theory.

The great advantage of DFT over other, say Hartree–Fock-based, methods, is that it does not require too much computational effort to include the effects of electronic correlation in the calculation, which is known to be very important in obtaining reliable energies of chemical bonds. All it takes is an improved functional using the same set of Kohn–Sham orbitals, whereas the Hartree–Fock-based methods can only account for electronic correlation by considerably increasing the number of wave functions, leading to very long computation times for even the smallest system sizes. This makes DFT the method of choice for handling large systems, such as adsorbates interacting with surfaces.

The most popular series of functionals used in computational chemistry are those based on the generalized gradient approximation (GGA). These functionals include not only the electronic density, but also its spatial derivative (gradient), in order to account more accurately for longer-ranged electronic correlation effects (though very long-ranged electronic correlation effects, such as Van der Waals forces, are not accurately treated within the GGA). This type of calculation is often referred to as DFT-GGA. Various DFT-GGA functionals are available; some popular ones have been tested in [4,7,8]. As mentioned, the accuracy of these methods is roughly 5–10%.

Because extended surfaces and even nanoparticles are large systems from the atomistic point of view, the question still arises of what kind of molecular ensemble

would constitute a reasonable model for the adsorbate-catalyst interaction. Here, essentially two different types of approaches have been taken. One approach is to model the surface as a small cluster of atoms, where a typical cluster size is 10-50 atoms. It is important to note that this size is still smaller than that of a typical catalytic nanoparticle, which consists of at least several hundreds of atoms (and usually more)[9]. A second approach that has become popular in the last 10 years is to model the surface as a periodic slab, in which a certain ensemble is periodically repeated in three dimensions by applying periodic boundary conditions in the computational setup. A surface, and a molecule-surface ensemble, is then modeled as a number of layers (typically 3–5 layers) of atoms in one part of the periodic cell, and a vacuum in the other part of the cell. The vacuum region is chosen large enough such that the different periodic images of the surface have a negligible interaction with each other. One final comment to be made about clusters and slabs concerns the different types of basis sets in which the Kohn-Sham orbitals are expanded. Cluster calculations are usually carried out with a standard quantum-chemical package employing so-called localized basis sets. These localized basis sets enable one to interpret the Kohn-Sham orbitals as molecular orbitals as introduced in quantumchemical molecular orbital theory [10]. This may have great advantages in obtaining a more chemistry-based understanding of binding trends. Slab calculations, on the other hand, usually employ so-called plane waves as their basis set, because of the periodicity of the simulation cell [11,12]. Plane waves are not localized, and hence it is more difficult (though not impossible) to obtain molecular orbital-type information. However, it is now generally agreed that slab calculations give more reliable quantitative results when the binding energetics of the molecule-surface interaction is concerned. More local information, such as binding distances and vibrational properties, may still be calculated with good accuracy using cluster models. We discuss these issues in some more detail in Section 1.3.

1.2.2 Ab Initio Molecular Dynamics

One very prominent development in DFT has been the coupling of electronic structure calculations (which, when the ground state is concerned, apply to zero temperature) with finite-temperature molecular dynamics simulations. The founding paper in this field was published by Carr and Parrinello in 1985 [13]. Carr and Parrinello formulate effective equations of motion for the electrons to be solved simultaneously with the classical equations of motion for the ions. The forces on the ions are calculated from first principles by use of the Hellman–Feynman theorem. An alternative to the Carr–Parrinello method is to solve the electronic structure self-consistently at every ionic time step. Both methods are referred to as ab initio molecular dynamics (AIMD) [14].

AIMD is still a very time-consuming simulation method and has so far mainly been used to study the structure and dynamics of bulk water [14,15], as well as proton transfer [16] and simple $S_N 2$ reactions in bulk water [17]. AIMD simulations are as yet limited to small system sizes and "real" simulation times of not more than a few picoseconds. However, some first applications of this technique to interfacial systems of interest to electrochemistry have appeared, such as the water–vapor interface [18] and the structure of the metal–water interface [19]. There is no doubt that AIMD simulations of electrochemical interfaces will become increasingly important in the future, and some first results are described in Section 1.4.2.

1.2.3 Molecular Dynamics

In classical molecular dynamics (MD) methods [20] the atoms and molecules in the system of interest interact through effective pair potentials, which may be obtained from previous ab initio electronic structure calculations. However, the quantum nature of the system is not explicitly taken into account, and the time evolution of the system is obtained by solving Newton's classical equations of motion. Averaging of the MD trajectories over a sufficiently long simulation period allows one to extract thermodynamic, dynamical, and other macroscopic properties. Depending on the system size (which can include up to several thousands of atoms) and the type of particles involved, typical "real" simulation times in classical MD studies can be as long as several nanoseconds. As we discuss in Section 1.4.1, MD simulations are of great value in investigating the role of solvent reorganization in electron-transfer reactions.

1.2.4 Monte Carlo

An alternative to the MD method in obtaining statistical averages is the Monte Carlo (MC) simulation method, which is based on an efficient sampling of lowenergy configurations rather than on generating a dynamical trajectory [20]. A drawback of the standard MC algorithm is that it does not give any dynamical information, though for certain purposes it may be a more efficient way of calculating thermodynamic properties.

A method closely related to the standard "Metropolis"-type MC algorithm is a simulation technique known as kinetic Monte Carlo or dynamic Monte Carlo (DMC). This method is especially useful for studying processes on lattices, such as, for instance, catalytic reactions taking place on the reaction sites of a catalyst surface. One first defines the adsorption rates, desorption rates, reaction rates, and diffusion rates of the various reactions and processes assumed to take place on the surface, quantities that may in fact be estimated from first-principles electronic structure calculations. Next, the evolution of the entire system is obtained by solving the so-called master equation using an MC-type algorithm [21-24]. The algorithm is designed such that the exact time dependence is obtained, i.e., that the subsequent configurations generated satisfy the correct detailed balance. As Section 1.5 shows, this method is very useful in obtaining the correct dynamic behavior of a reactive system from the elementary processes. There is no need to resort to statisticalmechanical approximation schemes such as the mean-field approximation [9] in which all rates are expressed in terms of average coverages. Such approximation schemes may break down severely if the catalyst surface is very inhomogeneous, for instance due to poor mixing of the reactants on the catalyst surface or to a low concentration of catalytically active sites, or when strong interactions between adsorbates exist. DMC is the method of choice for the microkinetic modeling of catalytic reactions on surfaces when ordering, island formation, and slow surface mobility are deemed important. Lattice sizes in DMC can be as large as 1000×1000 sites (corresponding to 1 million surface sites), whereas the "real" computation times obviously depend on the (lowest) rate constants but can span time scales from a few milliseconds to several minutes.

1.3 REACTIVITY AND CATALYST ELECTRONIC STRUCTURE

1.3.1 Modeling Small Particles

The role of particle size in catalysis and electrocatalysis is a subject of longstanding interest. It is not our intention here to discuss in detail the available experimental and theoretical literature. Extensive reviews on particle-size effects in gas-phase catalysis and electrocatalysis can be found in the papers of Henry [25] and Kinoshita [26], respectively. Also, several monographs, reviews, and conference proceedings discuss particle-size effects from experimental, theoretical, and computational points of view [9,27,28].

It is well known that the electronic properties of small metal particles depend on the particle size. The work function or cluster ionization potential is a most dramatic example of this effect. Knickelbein et al. [29] have shown that for Ni clusters consisting of 3 to 90 atoms the cluster ionization potential continues to change and for the largest particle size is still about 0.2 eV higher than the work function of an extended surface. There is, however, a growing awareness that changes in reactivity and chemisorption properties with particle size reflect a much more local phenomenon. Smaller particles have more edges and kinks than larger particles, and these local sites usually possess a reactivity that is substantially different from those of the terraces. Surface-science studies in UHV and electrocatalysis have convincingly demonstrated the special reactivity of defects, showing that in certain cases the catalytic reaction takes place only on step and defect sites.

These facts obviously raise the question of what constitutes the best computational model of a small catalytic particle. As catalysis is often a local phenomenon, a cluster model of the reactive or chemisorption site may give quite a reasonable description of what happens at the "real" surface [1,3,30]. However, the cluster should still be large enough to eliminate cluster edge effects, and even then one must bear in mind that the cluster sizes employed in many computational studies are still much smaller than real catalytic particles (say 10–50 versus 50–1000 atoms, respectively). Hence, a slab model of a stepped surface may provide a much more realistic model of the active site of a catalytic nanoparticle. Hammer [31,32] has carried out quite extensive DFT-GGA slab calculations of N2 and NO dissociation at stepped Ru and Pd surfaces, showing how the dissociation energy is significantly lower at the low-coordination step sites compared to terrace sites. The special reactivity of step sites for the dissociation of NO and N₂ has been demonstrated in several recent surface-science studies [33,34]. Also, the preferential adsorption of CO on step sites has been demonstrated in UHV [35], under electrochemical conditions [36], as well as by means of DFT-GGA slab calculations [37].

1.3.2 Catalytic Reactivity and the Periodic Table

Because a catalytic reaction generally consists of a series of elementary steps, one of the key questions in understanding catalytic reactivity is which of these steps is ratelimiting. The rate-limiting step determines not only the overall catalytic activity, but often also the selectivity of the reaction. In search of an optimal catalyst, the overall rate of the reaction is often studied as a function of a certain "reactivity parameter" of the catalyst material. A typical "reactivity parameter" is the heat of compound formation, e.g., surface oxide formation, or the enthalpy of adsorption of what is believed to be a key intermediate. Plots of catalyst reactivity versus the reactivity parameter usually yield the well-known "volcano plots," the rationalization for which was first given by Sabatier [38]. The Sabatier principle essentially states that an active catalyst should adsorb a key intermediate neither too weakly nor too strongly. A weakly adsorbed intermediate has a low reactivity because of its low concentration, and a strongly adsorbed intermediate leads to a low reactivity because of the difficulty with which it can desorb. An intermediate interaction strength often leads to the optimum activity and selectivity.

There are innumerable examples of volcano plots and the Sabatier principle in catalysis, as we have recently elaborated in relation to heterogeneous gas-phase catalysis [2]. An illustrative recent example of the Sabatier example in electrocatalysis is the ammonia oxidation in alkaline solution [39]. The selectivity of the ammonia electro-oxidation toward N₂ is determined by the stability and concentration of hydrogenated nitrogen adsorbates NH_x (x = 1,2), as the atomic nitrogen adsorbate is inactive in producing N_2 at room temperature. As a result, metals that adsorb N strongly, such as Ru, Rh, and Pd, show no selective NH₃ oxidation, as the dehydrogenation capacity of these metals is too high, leading to a fully inactive N_{ad} covered surface. Coinage metals such as Cu, Ag, and Au show very little dehydrogenation capacity, and hence no activity for ammonia oxidation under electrochemical conditions. Only Pt and Ir, which show an intermediate dehydrogenation capacity, are able to oxidize ammonia to N2 with a reasonable steady-state activity. The dehydrogenation capacity may be related to the chemisorption energy of atomic nitrogen: a high adsorption energy would imply a high dehydrogenation capacity.

Given the importance of the Sabatier principle in catalytic science, the question arises about whether the reactivity parameter, usually the chemisorption energy of some key intermediate, can be related to a more fundamental property of the catalyst surface. In particular, one would like to make a connection between the reactivity parameter and the properties of a metal or alloy surface as they can be deduced from the periodic table. An important development along these lines has been a model proposed by Hammer and Nørskov [3,40]. Their model singles out three surface properties contributing to the ability of the surface to make and break Adsorbate bonds: (1) the center ε_d of the d-band; (2) the degree of filling f_d of the d-band; and (3) the coupling matrix element V_{ad} between the adsorbate states and the metal dstates. These quantities have been calculated from extensive DFT calculations for a significant portion of the periodic table. The basic idea of the Hammer–Nørskov model is that trends in the interaction and reactivity are governed by the coupling of the adsorbate states with the metal d-states, since the coupling with the metal spstates is essentially the same for the transition and noble metals.

Hammer and Nørskov have tested their model quite extensively [3] and have shown a good semiquantitative agreement between their model for the d contribution of the adsorption energy and the DFT-computed total adsorption energy of atomic adsorbates such as oxygen and hydrogen and molecular adsorbates such as carbon monoxide. Also, the activation energy, and hence the reactivity, of hydrogen dissociation onto various metal surfaces is described semiquantitatively by their model. Significantly, many of the observed variations among the different metals can be traced to variations in ε_d , and the hence total adsorption energy varies as $E_{ads} \sim \gamma \varepsilon_d$. Shifts in the (local) d-band energy, and hence variations in reactivity, can be brought about in a number of different ways. Variations in ε_d occur at steps and defects (see previous section), by alloying, or by making an overlayer system. We make use of this "d-band shift model" in the next section.

1.3.3 Hydrogen and Carbon Monoxide Adsorption on (Bi)metallic Surfaces

Alloy surfaces are of substantial importance in catalysis, such as in the hydrogenation of unsaturated hydrocarbons, Fisher–Tropsch synthesis, steam reforming of methane, and many other processes [41]. In electrocatalysis, they have recently received attention in relation to the development of CO-tolerant fuelcell catalysts [42]. In many of these processes, atomic hydrogen and carbon monoxide are the most important intermediates or poisons; therefore, these two adsorbates have received a great deal of attention in theoretical and computational studies.

Pallassana and Neurock [43–44], for example, use periodic DFT calculations to examine the chemisorption of hydrogen over different Pd_xRe_{1-x} surfaces in order to understand the properties that control chemisorption over these alloys. The results for hydrogen adsorption over the bare Pd and Re surfaces along with pseudomorphic overlayers of Pd on Re(0001) and Re on Pd(111) are presented here in Figure 1 [43]. The binding energy for atomic hydrogen is significantly



Figure 1 Adsorption of atomic hydrogen on Pd–Re model surfaces. (a) pure Pd(111), (b) pure Re(0001), (c) monolayer of Re on Pd(111), and (d) monolayer of Pd on Re(0001). (Adapted from Ref. [43].)

stronger on Re than it is on Pd. Re lies much further to the left in the periodic table and therefore has a much more open d-band. Re, therefore, contains more vacant states near the Fermi level that can accommodate electron transfer from the adsorbed hydrogen, thus leading to a stronger binding energy. The d-band center model proposed by Hammer and Nørskov [40] suggests that there should be an increase in orbital overlap since the center of the d-band shifts closer to the Fermi level. In addition, Pauli repulsion is reduced as we move from Pd to Re since Re has fewer filled states. Depositing an atomic layer of Re over Pd(111) or Pd over Re(0001) creates ideal pseudomorphic Re_{ML}/Pd(111) and Pd_{ML}/Re(0001) surfaces that have unique properties due to the degree of charge transfer between the two metals. The density of states projected onto the d-states at the top metal layer of Pd(111), Re(0001), Pd_{ML}/Re(0001), and Re_{ML}/Pd(111) were calculated in order to probe the electronic properties for each of these surfaces [43]. The results, which are shown in Figures 2 and 3, indicate that Pd and Re form a very strong bond at the Pd-Re interface of the Pd_{ML}-Re(0001) surface. An analysis of the density of states shows a significant shift of the d-band well below the Fermi energy. The density of states near the Fermi level looks quite similar to that of bulk gold. This would suggest that adsorbates should bind much more weakly on a the Pd_{ML} -Re(0001) surface than those on the pure Pd or pure Re surfaces. Indeed, the binding energy decreases from 2.77 to 2.35 eV as we move from Pd_{ML}/Pd(111) to Pd_{ML}/Re(0001). As we move to the Re surfaces, we find that there is little change in the hydrogen adsorption energies. The binding energy of hydrogen on Re is sufficiently strong that there is basically no change as we move from $Re_{ML}/Re(0001)$ to $Re_{ML}/Pd(111)$. The calculated binding energies for hydrogen on these surfaces correlated very well with the d-band center of the surface layer. The results are shown in Figure 3.

All the trends from these pseudomorphic studies readily fall out of the d-band center model. Pallassana and Neurock have shown that this model can be extended to predict what will happen over the alloyed surfaces as well [44]. In general, the hydrogen binding energy increases as the level of Re in the Pd surface layer is increased over the Pd(111) slab and decreases as the amount of Pd in the Re surface increases over the Re(0001) slab. Modeling the effect of the alloy, however, requires that we distinguish between Pd and Re adsorption sites since the energies on these metals are quite different. A weighted d-band model of the surface was therefore defined in order to account for differences between Pd and Re. The weighted d-band model is given in Eq. (1):

$$\epsilon_{d-\text{weighted}} = \frac{\left(V_{\text{Re}}^2 \cdot \epsilon_d^{\text{Re}} \cdot N^{\text{Re}} + V_{\text{Pd}}^2 \cdot \epsilon_d^{\text{Pd}}\right)}{\left(V_{\text{Re}}^2 \cdot N^{\text{Re}} + V_{\text{Pd}}^2 \cdot N^{\text{Pd}}\right)}$$
(1)

 V^2 here refers to the d-band coupling matrix element for the surface metal atoms, whereas N^{Re} and N^{Pd} refer to the number of Re–H and Pd–H bonds, respectively [44].

Hydrogen adsorption was examined on a series of alloyed surfaces including $Re_{ML}/Pd(111)$, $Pd_{33}Re_{66ML}/Pd(111)$, $Pd_{66}Re_{33ML}/Pd(111)$, $Pd_{ML}/Pd(111)$, $Pd_{ML}/Pd(111)$, $Pd_{ML}/Pd(111)$, $Pd_{ML}/Re(0001)$, $Pd_{66}Re_{33ML}/Re(0001)$, $Pd_{33}Re_{66ML}/Re(0001)$, and $Re_{ML}/Re(0001)$. The calculated hydrogen-binding energies on these surfaces are given in Figure 4. The weighted d-band model appears to capture most of the changes to the electronic structure. A plot of the weighted d-band against the DFT calculated binding energies



Figure 2 The density of states projected to the d-band of Pd–Re model surfaces. Solid line refers to the DOS projected to the d-band of the top layer. The dotted line refers to the second layer. (a) pure Pd(111), (b) $Pd_{ML}/Re(0001)$, (c) Re(0001), and (d) $Re_{ML}/Pd(111)$. The center of the d-band for each surface is depicted by the arrow. (Adapted from Ref. [43].)

on these alloyed surfaces indicates that this model works quite well for predicting binding energies over the PdRe alloys (Fig. 5). Some of the outlier points are systems where the most favored binding site changed due to a change in the surface composition. On the $Pd_{33}Re_{66}$ surface, for example, Pd acts to isolate smaller Re dimers structures. These dimers are unique. They behave like site-isolated Re clusters and therefore bind hydrogen more strongly. This would readily explain the deviations from the simple d-band center model.

The adsorption of carbon monoxide on metal surfaces can be qualitatively understood using a model originally formulated by Blyholder [45]. A simplified molecular orbital picture of the interaction of CO with a transition metal surface is given in Figure 6. The CO frontier orbitals 5σ and $2\pi^*$ interact with the localized d metal states by splitting into bonding and antibonding hybridized metal-



Figure 3 The binding energy of atomic hydrogen at the 3-fold fcc site on the Pd–Re surfaces as a function of the d-band center relative to the Fermi energy. (Adapted from Ref. [43].)

chemisorbate orbitals, which are in turn broadened by the interaction with the much more delocalized sp metal states.

Hammer et al. [46] show how this simple picture emphasizing the interaction of the CO frontier orbitals with the metal d-states can explain trends in the binding energies of CO to various (modified) metal surfaces. Generally, CO binds stronger to the lower transition metals (i.e., toward the left in the periodic table), mainly due to the center of the d-band ε_d moving up in energy, leading to a stronger back donation. The same Blyholder model may also be used to explain why on metals in the upperright corner of the periodic table (Pd, Ni) CO prefers multifold coordination, whereas toward the lower left corner (Ru, Ir) CO preferentially adsorbs atop (although steric considerations also play an important role in the argument) [47].

Of special interest to fuel-cell catalysis is the adsorption of CO to Pt-based bimetallic surfaces, in particular Pt–Ru. These surfaces have long been known to be considerably more active in the electrochemical CO oxidation than pure Pt or Ru. They are also more CO-tolerant hydrogen oxidation catalysts and better methanol oxidation catalysts for use in low-temperature fuel cells. Watanabe and Motoo [48] suggest a bifunctional mechanism to explain the unique reactivity of Pt–Ru surfaces. In their mechanism, the oxygen species with which CO reacts, presumably chemisorbed OH formed from the dissociative water oxidation, is preferentially formed on the Ru sites. The active site is a Pt–Ru pair with CO on Pt reacting with OH on Ru. Dynamic Monte Carlo simulations of this mechanism, showing the importance of CO mobility [49], are discussed in Section 1.5.2. Although the higher oxophilicity of Ru compared to Pt renders the bifunctional mechanism a reasonable assertion, it does not take into account any changes in the CO binding properties to the Pt–Ru surface compared to pure Pt or Ru.

We have recently carried out extensive slab calculations of CO and OH interacting with Pt-Ru surfaces [50,51]. Results from both our groups show that on the surface of a bulk alloy the CO binding to the Pt site weakens whereas that to the Ru site gets stronger. For example, on the surface of a homogeneous $Pt_2Ru(111)$ alloy, the CO atop binding to Pt is weakened by about 0.2–0.3 eV and that to Ru strengthened by about 0.1 eV. However, real catalytic surfaces are not homogeneous but may show the tendency to surface segregate. Figure 7 shows the binding energy and vibrational properties of CO to an atop Pt site on a series of surfaces with a pure Pt top layer, but for which the bulk composition changes from pure Pt, to Pt:Ru 2:1, to Pt:Ru 1:2, to pure Ru. It is observed that a higher fraction of Ru in the bulk causes a weakening of the CO bond to the Pt overlayer. This electronic alloying effect can be understood on the basis of the Hammer-Nørskov d-band shift model. Alloying Pt with Ru causes a downshift of the local d-band center on the Pt sites because the flow of electrons from Pt to Ru lowers the local d-band on Pt in order to maintain local electroneutrality. Interestingly, Figure 7 also illustrates that there is no correlation between the binding energy and the C–O stretching frequency, even though such a correlation is often assumed in the literature. On the other hand, the Pt–C stretching mode correlates well with the binding energy: a stronger bond causes the expected increase in the Pt–C frequency.



Figure 4 The binding energy of atomic hydrogen at the most favorable sites on Pd–Re alloyed surfaces: (a) $Re_{ML}/Pd(111)$, (b) $Pd_{33}Re_{66ML}/Pd(111)$, (c) $Pd_{66}Re_{33ML}/Pd(111)$, (d) Pd(111), (e) $Pd_{ML}/Re(0001)$, (f) $Pd_{66}Re_{33ML}/Re(0001)$, (g) $Pd_{33}Re_{66ML}/Re(0001)$, and (h) $Re_{ML}/Re(0001)$. (Adapted from Ref. [43].)



Figure 5 A comparison of the binding energy of atomic hydrogen at the most favorable adsorption sites on the Pd–Re alloyed surfaces and the d-band center relative to the Fermi energy. (Adapted from Ref. [44].)



Figure 6 Model of the orbital interaction diagram for CO adsorbed on transition-metal surfaces. (Adapted from Ref. [47].)



Figure 7 The binding energy, C–O stretching frequency ω_{C-O} , and Pt–C stretching frequency ω_{Pt-C} on four different surfaces, all with a surface layer of Pt, but different bulk compositions (Pt, Pt₂Ru, PtRu₂, Ru). (Adapted from Ref. [51].)

The opposite effect is observed when a surface with a pure Ru overlayer is considered, and the bulk is stepwise enriched with Pt. The CO binding to the Ru overlayer is strengthened with a higher content of Pt in the bulk. In fact, the Ru/Pt(111) surface is the one that shows the strongest CO binding. A similar effect is also observed when the top layer of a Pt(111) surface is mixed with Ru, leading to a surface alloy. As the Ru content of the surface layer increases, the binding to the Pt surface sites is weakened and to the Ru surface sites is strengthened.

The binding of OH to Pt–Ru surfaces shows trends that are quite similar to CO. In general, those surface sites that bind CO strongly (which are usually rich in Ru) also show a strong OH binding, and those surface sites that bind CO weakly (which are usually rich in Pt) also show a weak OH binding. This raises the question of whether Pt–Ru is a good example of a truly bifunctional catalyst with one surface component adsorbing one reactant and the other surface component the other reactant. In fact, on the basis of their extensive experimental investigations, the

Berkeley group has suggested that Pt–Sn and Pt–Mo alloys may constitute better examples of bifunctional catalysts [52]. Indeed, our most recent DFT-GGA slab calculations [53] show that on these surfaces CO may preferentially bind to Pt, whereas OH prefers to bind to Sn or Mo.

1.3.4 Electric Field Effects on CO Adsorption

One effect of special interest to electrochemists is the potential-dependent chemisorption of ions and molecules on electrode surfaces. A particularly well-studied example is the adsorption of CO on platinum single-crystal electrodes. In collaboration with the Weaver group at Purdue, we have recently undertaken detailed DFT calculations of the potential-dependent chemisorption of CO on platinum-group (111) surfaces [47,54,55], modeled as clusters, for comparison with the extensive vibrational characterization of these systems as carried out by the Purdue group [56,57]. The electrode potential in these studies is modeled as a variable external electric field applied across the cluster, an approach many others have taken in the past.

Two issues are of interest in relation to the potential-dependent bonding of CO to transition-metal surfaces: the potential-dependent binding energy and the resulting potential-dependent site preference; and the potential-dependent vibrational properties, in particular the internal C–O stretching frequency and the metalchemisorbate Pt–CO stretching mode. Figure 8 shows the effect of the applied field on the binding energy of CO in a onefold (atop) and multifold (hollow) coordination on a 13-atom Pt cluster. What is particularly significant in this figure is the change in site preference predicted by these calculations, from atop coordination at positive



Figure 8 Field-dependent binding energy plots, and constituent steric, donation, and back donation components, for CO adsorbed atop and hollow on a 13-atom Pt (111)-type cluster. The orbital components are plotted with respect to their zero-field values. 0.01 field a.u. corresponds to 0.514 V/Å. (Adapted from Ref. [54].)

fields to threefold coordination at negative fields. Qualitatively, such a potentialdependent site switch is indeed observed experimentally [56,57]. By decomposing the binding energy in steric and orbital contributions, and deconvolving the contributions of the different Kohn–Sham orbitals according to the different symmetry groups, it can be appreciated that the main factor driving this preference for multifold coordination toward a negative field is the back donation contribution. This increasing importance of back donation with a more negative field can be understood on the basis of the classical Blyholder picture. A more negative field implies an upward shift of the metal electronic levels with respect to the chemisorbate $2\pi^*$ orbital, leading to an enhanced back donation of metal electrons. Since the interaction of the metal with the $2\pi^*$ orbital is a bonding interaction, and bonding interactions tend to favor multifold coordination, CO will favor multifold adsorption sites at negative fields.

The change in the intramolecular C–O stretching mode with electrode potential has also been a subject of longstanding theoretical interest and has become known as the interfacial Stark effect. Important theoretical contributions in this field have been made by Lambert, Bagus, Illas, Curulla, and Head-Gordon and Tully [58-62]. We have recently reexamined this issue in the context of a detailed comparison of DFT calculations with the spectroscopic data of CO and NO adsorbed on a variety of single-crystalline transition-metal electrodes [47]. These calculations have confirmed that NO generally possesses a higher Stark tuning slope (i.e., change in C-O stretching mode with potential) than CO and that multifold CO exhibits a higher Stark tuning slope than atop CO. In agreement with earlier calculations, a decomposition analysis shows that the lowering (blueshift) of the internal C-O stretching mode upon adsorption is mainly due to the back donation contribution, as metal electrons occupy the $2\pi^*$ antibonding orbital of CO [63,64]. This back donation contribution is offsetting the steric contribution, also known as the "wall effect," which by itself leads to a redshift upon chemisorption. Although the positive Stark tuning slope is also mainly the result of the back donation contribution, i.e., the negative field leading to enhanced back donation and hence a lowering of the C-O stretching mode, the different slopes found for the different metals and coordination geometries are generally found to be the result of a subtle interplay between back donation, donation, and steric effects [47].

The field dependence of the substrate-chemisorbate M–CO stretching mode has received much less attention as its low frequency makes it difficult to be observed by in-situ IR spectroscopy. However, recent advances in the preparation of transition-metal surfaces for surface-enhanced raman spectroscopy (SERS) have made it possible to study in some detail the potential dependence of this vibrational mode [65,66]. Our recent DFT calculations suggest that, if a sufficiently wide potential window is available, the M–CO mode on Pt, Pd, and Ir exhibits a maximum [55]. The M–CO Stark tuning slope is positive for (very) negative fields, and negative for positive fields. A charge and dynamic dipole analysis indicates that this behavior is at least partially related to the ionicity of the surface bond. Negatively charged adsorbates, such as chemisorbed Cl or CO at negative fields, exhibit a positive Stark tuning slope, whereas positively charged adsorbates, such as chemisorbed Na and CO at positive fields, exhibit a negative Stark tuning slope. Covalently bonded adsorbates, such as CO at intermediate electric fields, do not exhibit a strong dependence of surface bond vibration on the electric field, and in fact for these adsorbates the relationship between ionicity and Stark tuning slope is not one to one [67]. Hence, the potential dependence of the surface bond vibration may serve as a (semiquantitative) measure of the bond ionicity, provided the bond is indeed ionic enough. Experimentally, the Pt–CO vibration exhibits a negative Stark tuning slope, and the maximum predicted by the DFT calculations has yet to be observed experimentally.

1.4 THE SOLVENT IN ELECTRODE REACTIONS

1.4.1 Marcus Theory and Molecular Dynamics of Electrode Reactions

One major complication that distinguishes electrocatalytic reactions from catalytic reactions at metal–gas or metal–vacuum interfaces is the influence of the solvent. Modeling the role of the solvent in electrode reactions essentially started with the pioneering work of Marcus [68]. Originally these theories were formulated to describe relatively simple electron-transfer reactions, but more recently also ion-transfer reactions and bond-breaking reactions have been incorporated [69–71]. Moreover, extensive molecular dynamics simulations have been carried out to obtain a more molecular picture of the role of the solvent in charge-transfer processes, either in solution or at metal–solution interfaces.

In the Marcus theory, the electron-transfer act between a donor and an acceptor molecule is a radiationless event accommodated by a suitable nonequilibrium configuration of surrounding solvent molecules. Hence, the relevant reaction coordinate in electron-transfer reactions is a kind of collective solvent coordinate, more precisely defined as the electrostatic potential at the location of the accepting or donating redox species due to the prevailing configuration of polar solvent molecules. Clearly, the energy associated with creating these nonequilibrium configurations is a free energy, as a multitude of solvent configurations may correspond to one-and-the-same value of this electrostatic potential. The idea of this collective or generalized solvent coordinate is hence to map all different solvent configurations onto a single reaction coordinate.

More explicitly, we can consider the prototype of a simple electron-transfer redox reaction, the ferri/ferro couple:

$$Fe^{3+} + e^- \leftrightarrow Fe^{2+}$$
 (2)

at some inert electrode material such as gold. Figure 9 shows a typical free-energy surface. In the Marcus theory, the free-energy surface consists of two parabolic curves with minima at the equilibrium solvent configuration(s). At the equilibrium electrode potential, the free energies of the two minima are equal. The solvent fluctuates around the minimum, and when it reaches the intersection point of the two curves, an electron may be exchanged with the metal in a radiationless fashion. This is the electron-transfer equivalent of the Franck–Condon principle, as during the electron exchange at the crossing point the nuclei do not change their positions. Whether the electron transfer really occurs is determined by the adiabaticity of the process. Usually, if the reaction takes place sufficiently close to the electrode, the electron transfer will always take place and the reaction is adiabatic.



Figure 9 Free-energy curves for simple "outer-sphere" electron-transfer reactions. $\lambda/4$ is the activation energy at equilibrium, λ being the solvent reorganization energy.

The activation energy for electron transfer is thus determined by the free energy at the intersection point (i.e., the transition state), which in turn depends on the curvature of the parabolic curves. This curvature, traditionally denoted by the symbol λ (see Figure 9), is known as the solvent reorganization energy. In the formula originally given by Marcus, the solvent reorganization energy depends on the static and optical dielectric properties of the solvent, ε_{opt} and ε_s , and the radius *a* of the reactant(s). For a single ion reacting at an electrode, the Marcus formula reads

$$\lambda = \frac{e_0^2}{a} \left(\frac{1}{\varepsilon_{\text{opt}}} - \frac{1}{\varepsilon_s} \right) \tag{3}$$

where we have neglected the image interaction of the ion with the metal electrode. This expression assumes a linear response between the charge on the ion and the polarization induced in the surrounding solvent, resulting in the prediction that the reorganization energy depends only on the size of the ion and not on its charge. However, recent detailed MD simulations [72] have shown that this is not an accurate description, and the reorganization energy of multivalent ions is lower than that of uncharged species or ions of low valency with the same size. The main reason for this is the dielectric saturation occurring near strongly charged ions, which may be interpreted in an effective lowering of the static dielectric constant ε_s near the ion, leading to a lowering of λ according to Eq. (3). Strongly nonlinear solvent responses also occur in the transition from a neutral species to a singly charged species, as the ion–dipole interactions lower the effective radius *a* in Eq. (3). The effect is particularly strong for a negatively charged species than to a positively charged species [72].

Many technologically important electrochemical processes are more complicated than the simple electron transfer in the Fe^{3+}/Fe^{2+} couple, in which neither of the reactants is supposed to adsorb onto the electrode surface. Typically, however, reactants or products are adsorbed onto the electrode surface, or the electrontransfer act induces the breaking of a bond in the reacting molecule. It is quite clear that in these more complex situations the Marcus theory is expected to break down and a more detailed description of the solvent–reactant–metal interaction is required. It is in the understanding of these processes that molecular dynamics (MD) currently play a vital role.

The electron exchange between the relevant energy level on the reactant and the metal levels can be treated by a so-called Anderson–Newns model [73]. The interaction with the water solvent is treated by extensive MD simulations. In a sense, this represents a kind of highly simplified tight-binding MD. The energy barrier for electron transfer is calculated by so-called umbrella sampling techniques, which is a systematic way of sampling trajectories away from the equilibrium configurations [20]. The electron transfer itself is treated adiabatically.

We have applied this formalism to the simplest type of bond-breaking electrontransfer reaction at a metal electrode [71,74]. The type of reaction we have in mind is the reductive cleavage of an R-X molecule:

$$\mathbf{R} \cdot \mathbf{X} + \mathbf{e}^{-} \to \mathbf{R}^{\bullet} + \mathbf{X}^{-} \tag{4}$$

where typically \mathbb{R}^{\bullet} is some carbon-centered radical fragment and X^{-} a halide ion. The \mathbb{R} -X molecule is separated from the metal electrode surface by at least one layer of water molecules, in agreement with the experimental deductions from the Savéant group for the methylchloride reduction [75].

Assuming a simple Marcus-type model for the interaction with the solvent, one can derive an analytical expression for the potential (free) energy surface of the bond-breaking electron-transfer reaction as a function of the collective solvent coordinate q and the distance r between the fragments R and X [71,75]. The activation energy of the reaction can also be calculated explicitly:

$$\Delta G_{\rm act} = \frac{(\lambda + D_e + \eta)^2}{4(\lambda + D_e)} \tag{5}$$

where λ is the solvent reorganization energy, D_e the bond dissociation energy, and η the free energy of the reaction, i.e., the distance from the equilibrium potential ("overpotential"). Savéant, who originally derived Eq. (5), carried out extensive experiments to test its qualitative validity [75].

In order to test the (in)correctness of the Marcus solvent model, we have carried out extensive MD simulations of a bond-breaking electron-transfer reaction in water at a platinum electrode. Figure 10a shows the computer simulated potential energy surface obtained by a two dimensional umbrella sampling technique. Analysis of the results in Figure 10a brings to light two important effects of the solvent the Marcus model does not account for.

First, the presence of an additional minimum at r = 3 Å along the reaction path is clearly discernible in the computer-simulated contour plot. The small energy barrier between this minimum and the minimum at r = 6 Å is due to the molecularity of the solvent: there is a free-energy cost associated with the making of the hole between the two fragments in order to fit in a water molecule.

Second, we have analyzed the curvature of the computer-simulated potential energy surface by a parabolic fitting of the energy surface along the q solvent coordinate at various separation distances r, in order to investigate any possible rdependence of the effective solvent reorganization energy. The result is shown in Figure 10b and clearly shows that the "local" solvent reorganization energy depends both on the well (i.e., R–X or R[•] and X⁻) and the interfragment distance r. The


Figure 10 (a) Computer-simulated contour plot of the free-energy surface obtained by molecular dynamics for the methylchloride reduction on Pt(111) electrode. (b) The interfragment distance-dependent solvent reorganization energy extrapolated from the molecular dynamics simulations. The dashed line gives the Marcus solvent reorganization energy obtained by a local harmonic fit of the reactant well. (Adapted from Ref. [74].)

dashed line in Figure 10b shows the solvent reorganization energy as determined from a local harmonic fit to the reactant well. Hence, the comparison of the analytical theory [71] and the MD computer simulations [74] clearly demonstrates the important role of solvent molecularity and nonlinearity in the breaking of bonds at electrode surfaces. Both features are not incorporated in the traditional Marcus theory.

1.4.2 Effect of Water on Catalytic Reactions from DFT and AIMD Calculations

The presence of a protic solvent at the surface of a metal significantly alters the local environment at the surface. This can impact both chemisorption as well as surface reactivity. Modeling the effects of solution, however, presents a major challenge for first-principle methods. A variety of semiempirical models exist that use continuum methods to describe solvation effects directly in the Hamiltonian. Amovilli et al. [76] provide an elegant review of the recent advances of polarizable continuum models. These methods lead to the most efficient analyses of solvent effects. This approach has been used extensively in the area of modeling enzymes and proteins. The difficulty with this approach, however, lies in the empirical description of the solvent cavity. A second method for treating solvent effects involves the introduction of one or two explicit solvent molecules into the calculations. This approach has proven to be quite valuable in the area of modeling homogeneous catalytic systems and reactions in zeolites. Catalysis on surfaces, however, presents a more difficult challenge.

Desai et al. [77] extend this idea by adding between 8-26 explicit water molecules into a unit cell of first-principles DFT slab calculations. The vacuum layer essentially is now completely filled with solvent molecules. The layer thickness between the slabs, the unit cell size, and the number of explicit water molecules added are manipulated to maintain the appropriate density of liquid water at the surface. The water molecules that fill the vacuum region effectively form an extensive hydrogen-bonding network. The adsorption of water on Pd(111) in the presence of liquid water was examined to show the effect of solution on the chemisorption properties. The calculated structure and energetics are shown in Figure 11. Although there is only a small change in the structure of water molecules adsorbed at the surface, there is a much more dramatic change in heat of adsorption. In the gas phase, water adsorbs to Pd through the lone pair of electrons on oxygen. Water sits at an angle of 17% tilted from the surface normal. This is consistent with known experimental results for water adsorbed on Pd(100). Water molecules that adsorb directly on the Pd surface lie flat along the surface layer. The surface layer is subsequently stabilized by the formation of a hydrogen-bonding network that organizes in the water multilayers above the surface. Water rapidly begins to lose its orientation and structure (i.e., crystallinity) with respect to the metal in the layers of molecules that are farther removed from the surface. The changes in structure of water are shown in Figure 11. The resulting adsorption configuration found here is quite similar to the "bilayer" model proposed by Doering and Madey [78].



Figure 11 The adsorption of liquid water on Pd(111). The binding energy for water on Pd(111) in the vapor phase is 30 kJ/mol. The binding energy for liquid water is -2.5 kJ/mol. (Adapted from Ref. [77].)

The formation of a hydrogen-bonded network weakens the metal-oxygen bonds at the expense of forming hydrogen bonds with the neighboring water molecules in solution. The adsorption energy of water on Pd(111) is reduced from -30 kJ/mol to -2.5 kJ/mol as we move from the vapor phase to solution. Experimental results show a similar trend. The experimental binding energy for water on Pd(100) is estimated to be -43 kJ/mol in the vapor phase [79]. The experimental TPD results for multilayers of water on Ag(110) by Bange et al. [80] suggest that the strength of the multilayer water-water interaction is nearly the same as water-metal interaction. This would indicate a net binding energy of about zero on Ag(110) in the presence of water multilayers.

The presence of solution can dramatically affect dissociative chemisorption. In the vapor phase, most metal-catalyzed reactions are *homolyticlike*, whereby the intermediates that form are stabilized by interactions with the surface. Protic solvents, on the other hand, can more effectively stabilize charge-separated states and therefore aid in heterolytic activation routes. Heterolytic paths can lead to the formation of surface anions and cations that migrate into solution. This is directly relevant to methanol oxidation over PtRu in the methanol fuel cell. The metalcatalyzed route in the vapor phase would involve the dissociation of methanol into methoxy or hydroxy methyl and hydrogen surface intermediates. Subsequent dehydrogenation eventually leads to formation of CO and hydrogen. In the presence of an aqueous media, however, methanol will more likely decompose heterolytically into hydroxy methyl (-1) and H⁺ intermediates.

We used periodic DFT and ab initio (DFT) MD simulations to examine the activation of acetic acid over Pd(111) [77]. The results from both of these methods agreed quite well with one another. In the vapor phase, acetic acid dissociates to form a surface acetate intermediate and chemisorbed surface hydrogen. If carried out in the vapor phase over Pd(111), the overall reaction energy for this step was calculated to be +28 kJ/mol. The calculated charges on the acetate and hydrogen surface intermediates compared much more favorably with those calculated from a simple gas-phase *free-radical* reaction than with a gas-phase *ionic* reaction. This indicates that the reaction is more *homolytic*. The adsorbed acetate intermediate carries a charge of 0.20 units greater than the acetate free radical, while the hydrogen atom gains a charge of 0.14 units on adsorption.

In the presence of a water solution, the reaction now becomes *heterolytic* [77]. Acetate anions along with protons are formed. At a low temperature the acetate anions remain chemisorbed to the metal surface, whereas the protons migrate into solution one solvation shell away from the surface, thus forming $H_5O_2^+$ intermediates. The structure of the chemisorbed product state is shown in Figure 12. We clearly see the formation of the well-known double layer. Acetate anions form a layer of negatively charged layer at the surface, which is stabilized by the layer of $H_5O_2^+$ that sits directly above it. A Mulliken charge analysis indicates an excess negative charge of 0.55 units on the adsorbed oxygen atoms of the acetate groups as compared to the acetate species formed by the dissociation of acetic acid over Pd(111) in the vapor phase. In addition, the atomic hydrogen formed in the presence of water has a net positive charge of 0.26 units as compared to the hydrogen intermediate formed in the presence of water by the dissociation of acetic acid in the vapor phase. This suggests that the dissociation of acetic acid over Pd(111) is much more heterolytic in the presence of solvent molecules than in the vapor phase.



Figure 12 The adsorption of acetic acid on Pd(111) in the presence of a water solution. The binding energy for the acetate anion on Pd(111) in the vapor phase is -212 kJ/mol. The binding energy for acetate in the presence of a water solution is estimated to be +62 kJ/mol. (Adapted from Ref. [77].)

The dissociative adsorption of acetic acid therefore leads to

$$(CH_3COOH)_{ads/aq} \rightarrow (CH_3COO)^{-}_{ads/aq} + H^{+}_{ads/aq}$$
(6)

Interestingly, it was found that the acetate anion formed in this reaction was more stable in solution rather than on the surface. The anion, however, forms quite readily on the surface and appears to be rather stable.

Ab initio MD studies were carried out to help understand the elementary processes that occur at the metal-solution interface [77]. At temperatures less than 300 K, acetic acid decomposed on Pd, leaving an adsorbed acetate intermediate along with a proton in solution. Above 300 K, however, surface acetate recombines with a proton in solution to form acetic acid. Acetic acid is then displaced from the surface by water. Once the acetic acid finds its way into solution, it redissociates to form acetate and protons in solution that are now more efficiently stabilized by water. A series of snapshots that portray some of the images from the simulation is shown in Figure 13. These results were further corroborated with a more conventional transition-state search approach, which showed that desorption of acetate from the surface was an activated process. The process is quite complicated, involving the simultaneous breaking of the acetate-metal bond, the formation of an



Figure 13 Snapshots from an ab initio MD simulation (T = 300 K) of acetic acid on Pd(111) in the presence of water. (a) Acetate forms at the surface along with an H₅O₂+ intermediate adjacent to the acetate layer; (b) acetate species and protons react at the surface to form acetic acid; (c) water displaces acetic acid from the surface; (d) water adsorbs to the surface; (e) acetic acid rotates in solution toward the water layer; (f) acetic acid dissociates in solution to form acetate anions and protons in solution. (Adapted from Ref. [77].)

O–H bond, and the displacement of acetic acid by water. This is followed by the subsequent redissociation of acetic acid in solution phase. This is quite different than the gas-phase metal-surface reaction, which typically involves a nonactivated desorption process. Activated desorption processes in electrochemical systems are well known [69,70].

As was just outlined, the presence of a solvent can dramatically affect metalcatalyzed reaction chemistry. It is well established that polar solvents can enhance reactions that have a greater degree of charge separation in the transition state than in their reactant state. The solvent acts to stabilize the transition state over the reactant state. This effectively lowers the activation barrier. Solution effects are, therefore, of critical importance to electrocatalytic systems.

Desai and Neurock [81] use period DFT calculations along with ab initio (DFT) MD simulations in order to establish the effects of protic solvents on the hydrogenation of formaldehyde to methoxy and hydroxy methyl intermediates over Pd(111). Although this work was carried out in order to gain insight into solvent effects for selective hydrogenation reactions, it also has direct relevance to the oxidation of methanol since these two steps are simply the microscopic reverse reactions for the decomposition of hydroxy methyl and methoxy.

The activation barrier for the addition of hydrogen to either the carbon or the oxygen end of formaldehyde leads to the formation of methoxy and hydroxy methyl intermediates, respectively. The activation barriers for methoxy and hydroxy methyl

formation in the vapor phase over Pd(111) are 76 and 87 kJ/mol, respectively. In the presence of water, however, the activation barriers are reduced to 59 and 65 kJ/mol. Water stabilizes the negative charge that forms on the CH₃O and CH₂OH surface intermediates as well as the positive charge localized on the protons that form. The reaction path to the hydroxy methyl is slightly less favored.

Interestingly, the presence of a protic water solvent can actually play a direct role in mediating this chemistry. Desai and Neurock found that the lowest energy path was mediated through solution rather than over the surface. In the presence of water, atomic hydrogen can donate an electron to the surface to form a proton, which subsequently migrates through solution. The barrier is lowered to 42 kJ/mol. Water provides the medium for the formation and subsequent shuttling of the proton. The primary roles of Pd here are to anchor formaldehyde and also to dissociate H₂. This path is quite similar to those proposed for electrocatalytic systems, which involve the formation and transfer of protons.

Similar calculations that examine the effect of solution on the chemistry at the anode for both the hydrogen and the direct methanol fuel cells are currently begin carried out. While detailed studies on the effect of the potential dependence and solution effects have been studied, no one has begun to couple the two studies. It is clear that this will be very important for future efforts.

1.5 MONTE CARLO SIMULATIONS OF CATALYTIC REACTIONS

Dynamic or kinetic Monte Carlo methods have been used to simulate the catalytic surface chemistry for various different reaction systems. The vapor-phase oxidation of CO to form CO_2 , however, has been the most widely studied due to its simplicity as well as its general applicability. Pioneering work by Ziff [82] and Zhdanov [83] shows the formations of interesting phase transitions as a function of the kinetics and lateral interactions. Many subsequent studies by various other groups extend the basic models to cover more general features.

1.5.1 Ab Initio-based MC Simulations of Ethylene Hydrogenation

Ethylene hydrogenation serves as a model system for the hydrogenation of other olefin as well as aromatics. In addition, it is directly relevant to the selective hydrogenation of acetylenic intermediates from ethylene feedstocks. Hansen and Neurock [84,85] developed an ab initio-based dynamic Monte Carlo simulation to follow the pathways and associated kinetics over Pd and PdAu surfaces in order to understand the microscopic features that govern this chemistry. A comprehensive set of first-principles density functional theoretical calculations was performed to determine the binding energies for ethylene and all reaction intermediates, including ethyl, ethylidene, ethylidyne, along with the CH_x decomposition products [86]. The activation barriers for the critical steps for ethylene and ethyl hydrogenation were calculated by performing an detailed set of transition-state searches of the potential energy surface. A plot of the energetics associated with the elementary reaction steps is shown in Figure 14. These energies were all calculated at the zero coverage limit.

DFT calculations were also used to calculate lateral interactions between coadsorbed intermediates. These results cover only the interactions for specific arrangements of adsorbates examined. The number of conceivable reaction



Figure 14 The DFT calculated potential energy profile for ethylene hydrogenation over Pd in *the zero coverage limit*. The sequence involves the dissociative adsorption of H2, the adsorption of ethylene, the addition of hydrogen to form ethyl, and the addition of hydrogen to ethyl to form ethane. (Adapted from Ref. [84].)

environments that can form in the simulation, however, is on the order of hundreds of thousands. Therefore, while the ab initio calculations provide a start, they cannot calculate all the conceivable states. Instead, the ab initio results can be used to establish simpler models that can be called internally within the simulation. The DFT results calculated for the ethylene system were used to regress bond-order conservation and force-field models that were subsequently called "on the fly" in the simulation to calculate the through-space and through-surface interactions between adsorbates.

The simulation uses a variable-time step method in order to simulate the kinetics over different Pd and PdAu surfaces [85]. The temporal behavior of all intermediates is explicitly tracked throughout the simulation. All atop, bridge, and 3- and 4-fold hollow sites are specifically followed as a function of time. The simulation follows all lateral and through-space interactions between coadsorbed intermediates within a cut off of two nearest-nearest neighbors.

The simulation was used as a "virtual experiment" in order to monitor the surface coverage, the surface binding energies of all intermediates, along with the reaction rates. The simulation enables us to back out overall turnover frequencies as well as individual elementary step turnover frequencies (for hydrogen adsorption, ethylene hydrogenation, ethyl hydrogenation, and the desorption of products). The lateral interactions between coadsorbed intermediates proved to be quite important in dictating both the surface coverage as well as the reaction rate. Most of the interactions in this system were found to be repulsive. Repulsive interactions weaken the binding energies and act to lower hydrogenation barriers. The barriers for both ethylene and ethyl hydrogenation dropped from 15 kcal/mol for a surface coverage of 0 to about 9 kcal/mol for surface coverages that are greater than 0.3 ML.

calculated barriers here are in very good agreement with experimental results reported by Davis and Boudart [86]. Our simulation results were also taken at different partial pressures and used to establish the reaction orders for both ethylene and atomic hydrogen. These results are in remarkable agreement with those from experiment as is seen in Eqs. (7) and (8), especially considering that the simulation results were derived solely from first principles.

$$R_{\text{Ethane}}^{\text{Simulation}} = 10^{5.4 \pm 0.07} \exp\left(-\frac{9.5 \pm 2.5 \,\text{kcal/mol}}{RT}\right) P_{\text{H}_2}^{0.65 - 1.0} P_{\text{C}_2\text{H}_4}^{-0.4 - 0.0} \tag{7}$$

$$R_{\text{Ethane}}^{\text{Experiment}} = 10^{6.3 \pm 0.07} \exp\left(-\frac{8.5 \pm 2.5 \,\text{kcal/mol}}{RT}\right) P_{\text{H}_2}^{0.5-1.0} P_{\text{C}_2\text{H}_4}^{-0.3-0.0} \tag{8}$$

The simulations provide a full disclosure of how the atomic structure of the adsorbed layer changes with changes in processing conditions.

The direct accounting for atomic structure within the Monte Carlo algorithm enables one to explore how changes in the atomic arrangement of metal atoms at the surface impact kinetics and ultimately the slate of products produced. Mei et al. [87] extend their results on Pd to PdAu in order to examine the effects of alloying. They found that alloying has little impact on the overall rate of reaction. The turnover frequency on a per-palladium atom basis remained constant over various compositions of Pd and Au and various ensemble sizes. The results for various alloys are shown in Figure 15. These results are consistent with experimental results by Davis and Boudart [86], who show very little change in the turnover frequency as Au is alloyed with Pd.

The simulation results by Mei et al. [87] indicate that the invariance in turnover frequency is due to both geometric as well as electronic effects. A snapshot taken from the simulation of ethylene hydrogenation over $Pd_{93.5\%}Au_{6.25\%}$ is shown in Figure 16. The addition of Au into the surface lowers the number of sites for hydrogen activation. This leads to a lower surface coverage of hydrogen. This is purely a geometric whereby gold shuts down sites, which slows down the overall rate. This decrease in the rate, however, is offset by a relative increase in the rate due to the weaker interaction of ethylene and hydrogen on the alloyed surfaces. This weakening of the metal–adsorbate bond by alloying is purely electronic. The two effects balance one another out, whereby the overall turnover frequency relative to the number of Pd sites remains constant. Although the relative activity is insensitive to the alloy, there is a much more dramatic effect on the selectivity. Gold acts to shut down the larger surface ensembles that are necessary for the formation of the decomposition intermediates such as ethylidyne, CH, and carbon.

1.5.2 Electrochemical CO Oxidation on Pt–Ru Alloy Surfaces

Dynamic Monte Carlo simulations have been employed to study the effect of the bimetallic catalyst structure and CO mobility in a simple model for the electrochemical oxidation of CO on Pt–Ru alloy electrodes. The Pt–Ru surface was modeled as a square lattice of surface sites, which can either be covered by CO or OH, or be empty. The important reactions taken into account in the model reflect the generally accepted bifunctional model, in which the OH with which CO is

	Turn–over Frequency	H* Coverage (ML)	E _{ads} (H*) (kcal/mol)	E _{ads} (C ₂ H ₄ *) (kcal/mol)	C ₂ H ₄ * Coverage (ML)
Surface Alloy Composition	0.10	0.15	0.0	10.7	0.1875
	0.10	0.27	61.6	9.7	0.176
	0.13	0.25	62.3	9.3	0.184
	0.11	0.29	61.3	8.5	0.179
	0.13	0.27	61.3	10.3	0.176
	0.15	0.28	61.2	9.1	0.18
	0.14	0.36	62.1	9.1	0.19
	0.14	0.42	62.5	9.1	0.182

Figure 15 The effect of alloying Au with Pd on ethylene hydrogenation. The addition of gold shows little change with respect to the overall turnover frequency on a per-palladium site basis. Au reduces the hydrogen coverage but also weakens the adsorption energy of hydrogen.

supposed to react is preferentially formed on the Ru surface sites:

*

$$H_2O + \stackrel{\tau}{R_u} \leftrightarrow OH_{Ru} + H^+ + e^- \tag{9}$$

$$CO_{Ru} + OH_{Ru} \leftrightarrow CO_2 + H^+ + 2_{Ru}^* + e^-$$
(10)

$$CO_{Pt} + OH_{Ru} \leftrightarrow CO_2 + H^+ + {*}_{Pt} + {*}_{Ru} + e^-$$
(11)

The DMC simulations explicitly take into account the (finite) mobility of CO, by specifying the rate at which an adsorbed CO can exchange places with an empty site (or, more realistically, with a physisorbed water molecule):

$$CO_{Pt,Ru} + *_{Pt,Ru} \leftrightarrow *_{Pt,Ru} + CO_{Pt,Ru}$$
(12)

The rate of this reaction is proportional to the diffusion coefficient D.

The simulations were designed to mimic as closely as possible the experiments carried by Gasteiger et al. [88]. These authors prepared well-characterized Pt–Ru alloys in UHV before their transfer to the electrochemical cell. The surface consisted of a random mixture of Pt and Ru sites, onto which a saturated monolayer of CO was adsorbed. The monolayer was oxidized in a CO-free electrolyte by stripping voltammetry, and the catalytic activity of the Pt–Ru alloy was studied as a function



Figure 16 A single snapshot from the simulation of ethylene hydrogenation over the welldispersed $Pd_{93.5\%}Au_{6.25\%}$ alloyed surface. Ethylene adsorbs on both Pd and Au sites. Atomic hydrogen however prefers only the threefold *fcc* sites of Pd.

of the fraction of Ru sites on the surface. The lower the potential needed to oxidize the CO layer, the higher the catalytic activity of the surface.

In our DMC simulations, the Pt–Ru lattice was initially filled with CO up to 99%, with no preference for either site. The CO adlayer was oxidized at a series on randomly mixed Pt–Ru surfaces with varying Ru content. The resulting stripping voltammetry for high diffusion rates D is shown in Figure 17, and the dependence of the peak potential, at which the oxidation current reaches a maximum, as a function of Ru fraction and diffusion rate in Figure 18. (The motivation for the choice for the exact numerical values of the other rate constants can be found in the original paper.) It is clearly observed from Figure 18 that a relatively fast diffusion rate is necessary for the surface to show a significant catalytic enhancement. For fast diffusion, the optimum catalytic activity is observed at about 0.5 Ru fraction, in agreement with experiment. This optimum can be understood as being the result of a



Figure 17 CO stripping voltammetry from Dynamic Monte Carlo simulations, for pure Pt $(x_{Ru} = 0)$, various Pt–Ru alloy surfaces, and pure Ru. Details of the kinetic rate constants can be found in the original publication. CO surface diffusion is very fast, hopping rate *D* from site to site of 1000 s^{-1} . (Adapted from Ref. [49].)



Figure 18 CO stripping peak potential E_p from dynamic Monte Carlo simulations as a function of the Ru fraction on the Pt–Ru model surface, for three different surface diffusion rates D = 0, 1, and 1000 s^{-1} and for a mean-field model. (Adapted from Ref. [49].)

maximization of the number of Pt–Ru neighbors. More importantly, the DMC simulations for fast diffusion show that only a small fraction of Ru is needed to observe a major negative shift (about 200 mV) in peak potential. This fact is in excellent agreement with the stripping experiments of Gasteiger et al. Moreover, the shape of the stripping voltammetry shown in Figure 17, from relatively broad at low x_{Ru} , narrower at intermediate x_{Ru} , and broader again at the highest x_{Ru} , agrees very well with the experimental results. These results clearly suggest the importance of CO surface mobility in explaining the electrocatalytic activity of Pt–Ru alloys.

1.6 CONCLUSIONS

In this chapter we have described some recent applications of various computational methods to understanding some basic principles of complex catalytic and electrocatalytic processes. These methods rely on either quantum-mechanical or statistical-mechanical principles, or a combination of both, and obviously the level of detail and the kind of insight into a certain catalytic problem will depend on the chosen method.

Quantum-chemical electronic structure calculations, in practice usually DFT-GGA calculations, allow one to calculate binding energies and activation barriers of processes taking place on well-defined catalyst surfaces. From many detailed calculations, it can be concluded that many adsorption processes and surface reactions are controlled by the energy level of the d-band at the site where the process is taking place. We have illustrated how this model (or modifications thereof), suggested by Hammer and Nørskov, explains the basic binding-energy trends in the adsorption of hydrogen and carbon monoxide on PdRe and PtRu alloy surfaces. The field-dependent binding of carbon monoxide can also be described by a model in which the d-band shifts with respect to the carbon monoxide frontier orbitals as a result of the applied electric field. The DFT calculations also show that, unfortunately, the field-dependent or substrate-dependent vibrational properties of adsorbed CO are usually not good indicators of changes in the CO binding strength.

Finite-temperature molecular dynamics simulations are required to model the influence of the solvent on catalytic reactions taking place at electrified metal-liquid interfaces. In general, the presence of the solvent leads to charge transfer or charge separation across the interface, due to the charge-stabilizing properties of the polar solvent. The standard model for electron-transfer reactions is the classical Marcus model. Molecular dynamics simulations clarify the molecular role of the solvent reorganization accompanying charge-transfer reactions. In general, the solvent reorganization responds in a nonlinear fashion to changes in the charge on the reacting species, so that the Marcus continuum models are often not accurate. Effects of solvent molecularity, dielectric saturation, and electrostriction are important, especially when both neutral and charged species are involved in the reaction. Ab initio MD simulations also underscore the importance of charge stabilization in catalytic reactions at the metal-water interface. For the dissociation of acetic acid, it was found that at the metal-gas interface this reaction is homolytic because the interaction with the surface dominates, whereas it is rendered heterolytic at the metal-water interface due to the strong interactions with the protic solvent. Methanol decomposition on a Pd surface was also found to be strongly influenced by the water solvent. The solvent may lower the energy barrier of reactions that involve charged transition states or intermediates and may thereby change the lowest energy path when several possible pathways exist.

Finally, dynamic Monte Carlo simulations are very useful in assessing the overall reactivity of a catalytic surface, which must include the effects of lateral interactions between adsorbates and the mobility of adsorbates on the surface in reaching the active sites. The importance of treating lateral interactions was demonstrated in detailed ab initio-based dynamic Monte Carlo simulations of ethylene hydrogenation on palladium and PdAu alloys. Surface diffusion of CO on PtRu alloy surfaces was shown to be essential to explain the qualitative features of the experimental CO stripping voltammetry. Without adsorbate mobility, these bifunctional surfaces do not show any catalytic enhancement with respect to the pure metals.

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2

Simulations of the Reaction Kinetics on Nanometer-Sized Supported Catalyst Particles

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CHAPTER CONTENTS

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SUMMARY

The reaction kinetics on supported nm-sized catalyst particles may be quite different compared to those observed on macroscopic poly- or single-crystal surfaces, because

the very function of the catalyst is often affected by decreasing the particle size, due to inherent factors connected with the properties of small particles alone, or as a result of new kinetic effects arising on the nm scale. These proven or suspected differences between supported catalysts and macroscopic surfaces have long been recognized to be a central part of the so-called structure-gap and pressure-gap problems in catalysis. To bridge these gaps and to form a conceptual basis for the understanding of reactions occurring on supported catalysts, we summarize in the present review the results of simulations scrutinizing qualitatively new effects in the reaction kinetics on the nm scale. Attention is paid to such factors as reactant supply via the support, interplay of the reaction kinetics on different facets, adsorbateinduced reshaping of catalyst particles, selectivity on the nm scale, and oscillatory and chaotic kinetics on nm catalyst particles. The kinetics of the growth of nm particles is briefly discussed as well.

2.1 INTRODUCTION

Understanding of the kinetics of heterogeneous catalytic reactions (HCR) is of high practical importance because heterogeneous catalysis constitutes cornerstones for the chemical industry and environmental technologies [1]. Physically and chemically, the kinetics of HCR are of interest due to their richness and complexity related to such factors as adsorbate-substrate and adsorbate-adsorbate lateral interactions, surface heterogeneity, and/or spontaneous and adsorbate-induced surface restructuring [2-4] and manifested in such phenomena as chemical waves, kinetic oscillations, and chaos [2-9]. In basic academic studies, HCR are usually explored on macroscopic poly- or single-crystal surfaces. In practice, however, HCR often run on very small (≈ 10 nm) crystalline particles, deposited on the walls of pores of a more or less inactive support. The specific catalytic activity (i.e., the activity of an adsorption site) of such particles may be quite different compared to that of macroscopic samples. The collective set of such differences and the challenge to understand and explain them is referred to as the *structure (or materials) gap* in catalysis. An additional factor complicating bridging academic and applied studies is the pressure gap, expressing that practical conditions involve pressures of 1 atm or higher, while many of the most detailed academic studies have been performed at vacuum conditions, typically at 10^{-9} – 10^{-4} Torr.

The physics behind the structure gap is usually believed to be related with unique electronic properties of nm metal particles, contribution of the facet edges or other nonideal sites to the reaction rate, and/or so-called metal-support interaction [10]. These factors may also play a role for the pressure gap, which in addition is affected by the difference in population of adsorption sites at high and low pressures. The gaps may also be connected with the purely kinetic effects such as, e.g., the interplay of the reaction kinetics occurring on different facets [11] and spillover effects. All these effects are complicated by the fact that the adsorbate coverages at practical conditions are often appreciably higher than those inherent for surfacescience-based studies. Extrapolation of kinetic data from low- or moderate-coverage regimes to those with high coverages (for relevant discussion, see [12] and [13]) is not straightforward due to the nonideality of the HCR kinetics.

Despite the longstanding interest, understanding the factors behind the structure and pressure gaps is far from complete. This state of development is connected first of all with limited experimental information on both the structure and reactant populations of nm catalyst particles under reaction conditions. This problem can be experimentally addressed by applying more sophisticated physical methods of investigation to real porous catalysts and/or using various modern techniques aimed at preparation of model-supported catalysts consisting of wellcontrolled arrays of catalyst particles deposited on planar surfaces [11]. For very small particles, these methods are, e.g., carefully controlled evaporation and annealing of condensed particles, or deposition of clusters by cluster beams. The deposits can be characterized by scanning-probe techniques or electron microscopy even under reaction conditions. Such model systems were recently reviewed comprehensively by Henry [14]. For somewhat larger particles (≥ 10 nm), electronbeam lithography can be employed [15,16] to make nearly perfect arrays of supported particles. These experimental preparation techniques have demonstrated that it is possible to fabricate particle arrays of fairly uniform size and shape distributions, which can be varied systematically. Recent examples of using such arrays in catalytic studies can be found in [17–19].

In parallel with the experimental efforts, the pressure- and structure-gap problems can and should be addressed theoretically. In particular, using as an input the structural and kinetic data supplied by surface science, one can construct kinetic models of HCR running on nm particles. At present, the applicability of such models to specific real systems is usually limited, because the input data are, as a rule, incomplete. Nevertheless, this approach makes it possible (1) to clarify the conceptual basis of our understanding of the kinetics of HCR occurring on supported catalysts and (2) to use this information for planning and analysis of related experimental research. With the latter two points as primary goals, we have executed a series of simulations [20-30] aimed at identifying and quantifying novel, purely kinetic effects inherent to HCR on the nm scale. A detailed review of our simulations up to 1999 was recently published in Surface Science Reports [11]. The present paper briefly outlines the results reviewed earlier [11]. The simulations performed after [11] are discussed in more detail. [For a recent review of the meanfield (MF) and Monte Carlo (MC) treatments of the conventional (no nm specifics) kinetics of HCR, see [13] and [31], respectively.]

2.2 REACTANT SUPPLY VIA THE SUPPORT

Kinetics of HCR can be affected by adsorption of reactants on the support followed by diffusion to catalyst particles, and vice versa (spillover). In the case of CO oxidation, for example, the first experimental reports indicating that the CO supply via the support may be important for model nm catalysts, obtained by evaporating Pd onto mica, Al_2O_3 , SiO_2 , and MgO(100), were published in the 1980s (see the reviews [14,32]). On the noble metals, this reaction runs via the standard Langmuir–

Hinshelwood mechanism,

$$CO_{gas} \rightleftharpoons CO_{ads}$$
 (1)

$$(O_2)_{gas} \rightarrow 2O_{ads} \tag{2}$$

$$CO_{ads} + O_{ads} \rightarrow (CO_2)_{gas} \tag{3}$$

Additional steps related to CO adsorption on the support are especially significant when the relative CO pressure is low and the reaction occurs far from the CO adsorption-desorption equilibrium. In this limit, the contribution of the supportmediated steps to the reaction rate was analyzed qualitatively by Boudart and coworkers [33] by using the "collection zone" concept and quantitatively by Henry [34] by employing the MF reaction-diffusion (RD) equations. In the latter treatment, CO diffusion jumps from the support to the metal were considered to be rapid and irreversible (mathematically, this means that the CO coverage on the support in the vicinity of the catalyst boundaries was assumed to be zero). A more general MF analysis [20] of the problem includes treatment of all the elementary steps with selfconsistent boundary conditions. The catalyst particles are considered to be regularly distributed on the support. Typical reaction kinetics obtained in the case when the CO diffusion (collection) zones around different catalytic particles are not overlapping (i.e., the particles are sufficiently far apart) are shown in Figure 1 together with the conventional kinetics when there is no CO supply via the support. Due to the support-mediated CO adsorption, the position of the maximum reaction rate is seen to be shifted to a lower value of the relative CO pressure, $P_A/(P_A + P_B)$. In addition, the dependence of the reaction rate on the reactant pressure (for the regime where $P_{\rm CO}$ ($P_{\rm CO} \equiv P_A$) is small and the surface is predominantly covered by oxygen) is changed considerably (it becomes almost linear) compared to the case without CO diffusion from the support. With increasing CO pressure, the system exhibits a transition from a regime where the reaction rate is almost completely controlled by CO supply from the support to a regime where diffusion from the support is negligible.

Note that the CO supply from the support-from a practical point of viewhas a negative effect. It makes the self-poisoning transition to a CO-covered surface to occur more easily than without the support channel. A situation where the support would instead supply oxygen would have a positive effect. The latter occurs on ceria, which is an example of practical importance of the reactant supply via the support. The Pt-on-ceria system may operate in car exhaust catalysts in the so-called oxygen-storage regime when a metal oxide (e.g., ceria) provides an oxygen uptake/ release function for reactions occurring on the noble metal catalyst [35,36]. An equally important and similar process is temporary NO_x storage in Pt-BaO structures where NO is oxidized to NO₂ on Pt (in O₂ excess) and stored as $Ba-NO_x$ species, until the reverse process of NO₂ release from $Ba-NO_x$ occurs, where NO₂ is reduced to N₂, during transient reducing conditions [37]. Understanding such processes is yet far from complete (see, e.g., the discussion in [38]) but can in principle be treated along the same line as the CO-spillover case. The difficulty is that at present the details of the oxygen (on ceria) and NO₂ (on BaO) transport and storage and the associated kinetic constants are too uncertain to allow detailed kinetic simulations.

2.3 INTERPLAY OF REACTION KINETICS ON DIFFERENT FACETS

The equilibrium geometric shape of nm catalyst particles is determined by the Wulff rule [39], stating that the shape is a consequence of minimizing the total surface free energy (for application of this rule during the adsorption–desorption equilibrium, see, e.g., [40]). Practically, this means that catalyst particles of fee metals contain primarily the (111) and (100) facets. The total rate of reaction occurring on such particles is often believed to be a sum of the reaction rates corresponding to independent facets. During catalytic reactions, adjacent facets can, however, communicate with each other by reactant diffusion. Physically, it is clear that this communication is of minor importance if reaction runs near the adsorption–desorption equilibrium, because in this case the net diffusion flux will be negligibly low. For reactions occurring far from the adsorption–desorption equilibrium, in contrast, the diffusion-mediated facet–facet communication may dramatically change reaction kinetics. This was explicitly demonstrated in our MC simulations [21,25] of CO oxidation on nm catalyst particles. (For related MC simulations of CO oxidation on a field emitter tip, see [41,42].)



Figure 1 (a) Reaction rate and (b) reactant coverages for a rapid $2A + B_2 \rightarrow 2AB$ reaction under steady-state conditions. The solid and dashed lines respectively show the kinetics with and without A supply via the support. In both cases, the kinetics are bistable. During the highly reactive regime (at relatively low P_A), the surface is covered primarily by B, i.e. $\theta_A \ll \theta_B$. The regime with lower reaction rate (at relatively high P_A) occurs with CO domination on the surface ($\theta_B \ll \theta_A$). The results have been obtained for $P_A + P_{B2} = 0.01$ bar and T = 450 K with the kinetic parameters typical for CO oxidation on Pt, Pd, or Rh (for the details of calculations, see [20]). The insert on panel (a) displays the model used in calculations. (Redrawn from Ref. [20].)



Figure 1 Continued.

Below we illustrate [43] the importance of facet-facet communication by analyzing a kinetic model of oxidation of saturated hydrocarbons. As a specific example, we treat propane oxidation,

$$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O \tag{4}$$

on Pt under lean-burn conditions. This reaction is of high current interest because hydrocarbons are one of the constituents of exhaust gases. Of special interest is the reaction kinetics during oxygen excess, in view of the legislation-driven trend toward lean combustion. In this case, the reaction is considered to be limited by C_3H_8 chemisorption accompanied by breaking one of the C–H bonds formed by the central carbon atom [44],

$$(CH_3 - CH_2 - CH_3)_{gas} + O_{ad} \rightarrow (CH_3 - CH - CH_3)_{ads} + (OH)_{ad}$$
(5)

Concerted $CH_3-CH_2-CH_3$ chemisorption with the formation of $(OH)_{ad}$ seems to be more plausible compared to chemisorption resulting in the formation of H_{ad} , because the O-H bond is probably much stronger than the H-Pt bond. Subsequent reaction steps (after breaking the first C-H bond) are assumed to be rapid. Thus, adsorbed atomic oxygen is the dominant species under reaction conditions.

Surface-science-based studies indicate (see the discussion in [45]) that (1) the lateral interactions between oxygen atoms adsorbed on Pt are strong ($\approx 2-3$ kcal/mol) and (2) the oxygen sticking coefficient rapidly decreases with increasing oxygen coverage. Although this information is not sufficient to simulate the kinetics of C₃H₈ oxidation with no fitting parameters, it allows an estimate of the magnitude of the

effects modifying the Langmuir kinetics of O_2 and C_3H_8 adsorption at relatively high oxygen coverages inherent for the reaction under lean conditions. In particular, the model [45] taking into account adsorbate–adsorbate lateral interactions makes it possible to obtain natural understanding and explanation of the apparent reaction orders with respect to C_3H_8 and O_2 . The simulations [45] were executed for the simplest case when the catalyst surface is uniform, i.e., the specifics of nm particles were ignored. In our present treatment, the main findings obtained earlier [45] are used as inputs of a generic MF model focused on the interplay of the reaction kinetics on different facets of an nm catalyst particle.

The particle shape is considered to be a truncated pyramid (Fig. 2), with top and bottom (100) facets and (111) side facets, with the largest (100) facet attached to the support (such particles are often observed in experiments [39]). The reaction is assumed to occur primarily on the facets. The contribution of the facet edges is neglected.

If C_3H_8 oxidation is complete (CO₂ and H₂O are the final products) and oxygen desorption is negligible [the latter is the case at temperatures of practical interest (below 700–800 K)], the steady-state balance of adsorbed species is described as

$$W_{\rm O_2} = 5W_{\rm C_3H_8} \tag{6}$$

where W_{O_2} and $W_{C_3H_8}$ are the adsorption rates of O_2 and C_3H_8 , respectively. The factor of 5 on the right-hand part of this equation takes into account that one needs five O_2 molecules in order to convert one C_3H_8 molecule to CO_2 and H_2O .

Equation (6) is applicable both to single-crystal surfaces and nm particles. In both cases, one should first calculate the O_2 and C_3H_8 adsorption rates corresponding to the (111) and (100) surfaces. In our model, these surfaces are represented by triangular and square lattices, respectively. To describe the reactant adsorption kinetics on these lattices, we take into account that under the lean-burn



Figure 2 Pyramidal particle.

conditions Pt is covered primarily by atomic oxygen. The coverages of other species (including the propyl fragment) are considered to be negligibly low. With these conditions, the adsorption rates depend on the arrangement of adsorbed oxygen atoms, which in turn depends on oxygen–oxygen lateral interactions. In general, the interactions are rather complex [46]. For our goals, it is sufficient to take into account only nearest-neighbor repulsive interactions (Fig. 3), because these interactions dominate at the relatively high temperatures ($\approx 600 \text{ K}$) typical for catalytic C₃H₈ oxidation. At such temperatures, the statistics of adparticles can be described by employing the quasi-chemical (QC) approximation. In particular, the rate of O₂ adsorption is given by [45,47]

$$W_{\rm O_2} = k_{\rm O_2} \mathcal{P}_{\rm O_2} \mathcal{P}_{\rm 00} S^{2z-2} \tag{7}$$

where k_{O_2} is the adsorption rate constant on the clean surface, P_{O_2} is the oxygen pressure, \mathcal{P}_{00} is the QC probability that two nn sites are vacant, and

$$S = \frac{\mathscr{P}_{00} + 0.5\mathscr{P}_{A0}\exp(-\epsilon_1^*/k_{\rm B}T)}{\mathscr{P}_{00} + 0.5\mathscr{P}_{A0}}$$
(8)

is the factor taking into account the nonideality of adsorption (\mathcal{P}_{A0} is the QC



Figure 3 Schematic arrangement of adsorbed particles on a square lattice. Open circles show oxygen atoms. The dimer composed of filled circles represents the activated complex for O_2 adsorption. The dimer, consisting of a filled square and circle, represents the activated complex $[O-(C_3H_8)]^*$ for C_3H_8 adsorption [the circle and square represent O* and $(C_3H_8)^*$, respectively]. The dashed lines indicate lateral adsorbate–adsorbate interactions. (Redrawn from Ref. [45].)

probability that a pair of nn sites is occupied by one oxygen atom, ϵ^{*}_{1} is the nearestneighbor interaction in the activated state for O₂ dissociation, and z = 6 or 4 is the number of nearest-neighbor sites for adsorption on triangular and square lattices, respectively). The probabilities \mathcal{P}_{00} and \mathcal{P}_{A0} , defined by Eqs. (3.3.22)–(3.3.24) in [47], depend on oxygen coverage and the nearest-neighbor O–O interaction in the ground state, ϵ_1 . The power 2z - 2 in Eq. (7) is related to the number of sites adjacent to the two sites occupied by the activated complex formed during O₂ adsorption.

Assuming C_3H_8 adsorption to occur in a concerted way on a vacant site near an adsorbed oxygen atom so that the activated state includes this atom and taking into account only nn O–O lateral interactions in the ground and activated state, we have [45,47]

$$W_{C_{3}H_{8}} = k_{C_{3}H_{8}} P_{C_{3}H_{8}} 0.5 \mathscr{P}_{A0} V^{z-1}$$
(9)

where $k_{C_3H_8}$ is the coverage-independent rate constant, $P_{C_3H_8}$ the C₃H₈ pressure, and

$$V = \frac{\mathscr{P}_{AA} \exp[-(\varepsilon_1^* - \varepsilon_1)/k_{\rm B}T] + 0.5\mathscr{P}_{A0}}{\mathscr{P}_{AA} + 0.5\mathscr{P}_{A0}}$$
(10)

the factor describing the nonideality of adsorption (ε^*_1 is the O–O interaction in the activated state for C₃H₈ dissociation).

In the equations above, we have six parameters, k_{O_2} , $k_{C_3H_8}$, ϵ_1 , ϵ^*_1 , ϵ^*_1 , and z, for each surface. Not to obscure the main message, it makes sense to minimize the number of free parameters. Following this line, we employ the same rate constants k_{O_2} and $k_{C_3H_8}$ and interactions $\epsilon_1 = 3 \text{ kcal/mol}$ and $\epsilon^*_1 = 2 \text{ kcal/mol}$ for both surfaces. For ϵ^*_1 , we use 2 and 0 kcal/mol for the (111) and (100) faces, respectively. With these parameters, the O₂ and C₃H₈ adsorption rates are higher (Fig. 4) for the (100) face, because z and ϵ^*_1 are lower in this case. As we will see, these differences among the facets are sufficient to produce unique new kinetics, compared to the individual facets.

Solving Eq. (6) with explicit expressions for the O_2 and C_3H_8 adsorption rates makes it possible to calculate the reaction rate, which is identified below with the O_2 adsorption rate per site, i.e., $W_r \equiv W_{O_2}$. In particular, Figure 5 shows the reaction rates for the (111) and (100) surfaces. Using these rates and assuming the (111) and (100) facets to operate independently, one can obtain the reaction rate for a catalyst particle with noncommunicating facets. This approach yields (Fig. 6)

$$W_r = \alpha^{(1)} W_r^{(1)} + \alpha^{(0)} W_r^{(0)} \tag{11}$$

where $\alpha^{(1)}$, $\alpha^{(0)}$ ($\alpha^{(0)} \equiv 1 - \alpha^{(1)}$), $W_r^{(1)}$, and $W_r^{(0)}$ are the fractions of adsorption sites and reaction rates (Fig. 4) corresponding to the (111) and (100) surfaces [the subscripts (1) and (0) refer to (111) and (100), respectively].

In reality, the (111) and (100) facets communicate via oxygen diffusion. In this case, Eq. (6) can be read as

$$\alpha^{(1)}W_{O_2}^{(1)} + \alpha^{(0)}W_{O_2}^{(0)} = 5\alpha^{(1)}W_{C_3H_8}^{(1)} + 5\alpha^{(0)}W_{C_3H_8}^{(0)}$$
(12)

where $W_{O_2}^{(1)}$, $W_{C_3H_8}^{(1)}$, $W_{O_2}^{(0)}$, and $W_{C_3H_8}^{(0)}$ are the reactant adsorption rates per site on the



Figure 4 O₂ (top) and C₃H₈ (bottom) adsorption rates (normalized to $k_{O2}P_{O2}$ and $k_{C3H8}P_{C3H8}$) on the (111) and (100) surfaces as a function of oxygen coverage at T = 600 K [according to Eqs. (7) and (9), respectively].

(111) and (100) facets. These rates, given by Eqs. (7) and (9), depend respectively on the oxygen coverages, $\theta_{O}^{(1)}$ and $\theta_{O}^{(0)}$, of the (111) and (100) facets. To solve Eq. (12), we need a relation between these coverages.

At relatively high temperatures typical for C_3H_8 oxidation, oxygen diffusion is rapid compared to other steps (for the Arrhenius parameters for this process, see [21]). In this case, the relation between $\theta_O^{(1)}$ and $\theta_O^{(0)}$ is given by the grand canonical distribution, i.e., one should have

$$\mu^{(1)}(\theta_{\mathbf{O}}^{(1)}) = \mu^{(0)}(\theta_{\mathbf{O}}^{(0)}) \tag{13}$$

where $\mu^{(1)}$ and $\mu^{(0)}$ are the chemical potentials of oxygen on the (111) and (100) facets.



Figure 5 Reaction rate (normalized to $k_{O2}P_{O2}$) and oxygen coverage as a function of p ($p \equiv 5k_{C3H8}P_{C3H8}/k_{O2}P_{O2}$) for the (111) and (100) surfaces at T = 600 K.

For these potentials, the QC approximation yields [47]

$$\mu^{(1)}(\theta_{\rm O}^{(1)}) = k_{\rm B} T \ln \left[\frac{\theta_{\rm O}^{(1)} F^6(\theta_{\rm O}^{(1)})}{1 - \theta_{\rm O}^{(1)}} \right] \left($$
(14)

$$\mu^{(0)}(\theta_{\rm O}^{(0)}) = \Delta E + k_{\rm B} T \ln \left[\frac{\theta_{\rm O}^{(0)} F^4(\theta_{\rm O}^{(0)})}{1 - \theta_{\rm O}^{(0)}} \right]$$
(15)

where ΔE is the adsorption energy difference between the facets at low coverages, and

$$F(\theta_{\rm O}) = \frac{\mathscr{P}_{AA} \exp(\epsilon_1 / k_{\rm B} T) + 0.5 \mathscr{P}_{A0}}{\mathscr{P}_{AA} + 0.5 \mathscr{P}_{A0}}$$
(16)

is the factor taking into account lateral interaction.



Figure 6 Reaction rate (normalized to $k_{O2}P_{O2}$) for an nm catalyst particle with $\alpha^{(1)} = 0.8$ at T = 600 K. Solid lines 1, 2, and 3 show the results obtained by taking into account the interplay of the reaction kinetics on the (111) and (100) facets [Eqs. (12) and (13) with $\Delta E = 10$, 0, and -10 kcal/mol, respectively]. The filled circles correspond to the case when the (111) and (100) facets operate independently [Eq. (11)].

To use Eq. (15), we need ΔE . This parameter can be estimated from the O₂ temperature-programmed desorption spectra. Scrutinizing the spectra collected in [48], we obtain $\Delta E \simeq -10$ kcal/mol [the negative sign of ΔE means that oxygen adsorption is more favorable on the (100) face].

Employing Eqs. (12) and (13), we have calculated (Fig. 6) the specific rate of C_3H_8 oxidation on an nm catalyst particle for $\Delta E = 0$ and ± 10 kcal/mol. For $\Delta E = 0$ and +10 kcal/mol, the reaction rate is found to be nearly equal to the rate calculated by assuming the (111) and (100) facets to operate independently. In the most important case when $\Delta E = -10$ kcal/mol, the reaction rate is *much higher* than the former ones. To rationalize this interesting finding, we show the contribution of the (100) facet to the total rates of O₂ and C₃H₈ adsorption and also oxygen coverages, $\theta_{O}^{(1)}$ and $\theta_{O}^{(0)}$, of the (111) and (100) facets for $\Delta E = -10$ kcal/mol. In this case, oxygen adsorption is thermodynamically favorable on the (100) face and accordingly, due to oxygen supply from the (111) facet, the oxygen coverage of the (100) facet is higher than in the case of the independent (100) surface (cf. Figures 5 and 7). The oxygen coverage of the (111) facet is accordingly lower than in the case of the independent (111) surface. Under such circumstances inherent for an nm particle, the contribution of the (100) facet to the total rate of O_2 adsorption is nearly negligible, i.e., O_2 adsorption occurs primarily on the (111) facets. In contrast, C_3H_8 adsorption takes place almost exclusively on the (100) facet. The total rates of both these processes are higher than the corresponding rates for independent (111) and (100) surfaces, because the oxygen coverages of the (111) and (100) facets are respectively lower and higher than those of the independent surfaces. For these reasons, the



Figure 7 Ratio of the rate of O₂ adsorption on the (100) facet to the total rate of O₂ adsorption (open circles), similar ratio of the rates of C₃H₈ adsorption (filled circles), and oxygen coverages of the (111) and (100) facets of an nm particle as a function of *p* for $\Delta E = -10$ kcal/mol.

reaction rate on an nm particle is higher than that calculated by ignoring communication between the facets.

In summary, our analysis of the kinetics of C_3H_8 oxidation on nm-supported Pt particles shows that, due to the purely kinetic factors related to the interplay of the reaction kinetics on different facets, the activity of a catalyst particle may be appreciably higher than that calculated by assuming that the facets operate independently. This important effect, found to apply for a wide range of reactant pressures, may of course occur in many other catalytic reactions as well, since the underlying mechanism in the present analysis is generic.

2.4 PHASE SEPARATION ON THE NM SCALE

Phase separation or, more broadly, island formation in HCR is possible due to attractive adsorbate-adsorbate lateral interactions (thermodynamic mechanism)

and/or limited mobility of adsorbed species (kinetic mechanism). Under transient conditions, island formation has been experimentally observed (by using STM) in plenty of reactions [49]. Experimental data on island formation under steady-state regimes are, however, scarce. Theoretically, phase separation occurring due to attractive lateral interactions during the simplest A + B reaction under steady-state conditions was studied in [50–52]. The bulk of simulations was executed for the case



Figure 8 Arrangement of A molecules during the A + B reaction after reaching the steadystate regime. The reaction runs on a 100×100 lattice mimicking a pyramidal supported catalyst particle (Fig. 4). In the simulations, the top and side facets of the pyramid are represented by the central and peripheral sublattices of the lattice (A molecules, located on these sublattices, are shown by filled and open circles, respectively). Reaction occurs only on the central sublattice via the Eley–Rideal mechanism, including A adsorption on vacant sites and A consumption in collisions with gas-phase B particles. The peripheral sublattice is able to adsorb A. Attractive nn lateral interaction, introduced only for A molecules located on the central sublattice, is chosen so that $T=0.5T_c$. A diffusion on and between the sublattices is rapid compared to reaction. (Redrawn from Ref. [51].)

when reaction runs on a single-crystal surface. The case of supported catalyst particles was briefly treated [51] as well. For example, Figure 8 shows adsorbate distribution on a catalyst particle under the chemically reactive conditions at $T=0.5T_c$. Referring to an Ising model, one could expect that in this case all the facets were either free of or completely occupied by adsorbed particles. In contrast, the model predicts small islands formed on one of the facets. The island size depends on the interplay of reaction and phase separation.

2.5 OSCILLATIONS AND CHAOS

During the past two decades, regular and chaotic oscillations were found in about 30 reactions on practically all types of catalysts including single crystals, poly-crystalline samples (foils, ribbons, and wires), and supported catalysts over a pressure range from 10^{-12} bar to atmospheric pressure [2,5,6,8]. The experience accumulated indicates that oscillations are often observed in systems where a rapid bistable catalytic cycle is combined with a relatively slow "side" process, e.g., with oxide formation [53], carbon deposition [54], or adsorbate-induced surface restructuring [2,6]. Despite the fact that in many cases a mechanism of oscillations is considered to be established, the understanding of this intriguing phenomenon is still limited especially in the situations when the experiments are executed on supported catalysts (see, e.g., [55,56]). A few aspects of the latter problem were analyzed in our recent MC simulations [11,27–29].

The kinetics of CO oxidation on a pyramidal supported catalyst particle (Fig. 4) was simulated [11,27] by assuming CO adsorption to cause restructuring of the top (100) facet. The restructuring was described on the basis of the lattice-gas model, predicting phase separation in the overlayer. CO diffusion was much faster compared to other steps. Oscillatory and chaotic kinetic regimes were found in the simulations. One of the reasons of irregular oscillatory kinetics was demonstrated to be the interplay of the reactions on the (100) and (111) facets.

Oscillations connected with adsorbate-induced surface restructuring were studied also in [29]. The model used was aimed at mimicking oscillations in NO reduction by H_2 on a mesoscopic Pt particle containing two catalytically active (100) areas connected by an inactive (111) area that only adsorbed NO reversibly. NO diffusion on and between facets was much faster than other steps. The results obtained show that the coupling of the catalytically active sublattices may synchronize nearly harmonic oscillations observed on these sublattices and also may result in the appearance of aperiodic partially synchronized oscillations. The spatiotemporal patterns corresponding to these regimes are nontrivial. In particular, the model predicts that, due to phase separation, the reaction may be accompanied by the formation of narrow NO-covered zones on the (100) sublattices near the (100)–(111) boundaries. These zones partly prevent NO supply from the (111) sublattice to the (100) sublattices.

In the simulations [11,27,29] the size of a lattice representing a catalyst particle was relatively large [typically (100 \times 100)]. The effect of the lattice size on oscillatory kinetics was demonstrated [28] in simulations of CO oxidation accompanied by oxide formation. To mimic nm catalyst particles, the lattice size was varied from 50 \times 50 to 3 \times 3. With rapid CO diffusion, more or less regular oscillations were found (Fig. 9) for sizes down to 15 \times 15.

The simulations discussed above are focused on the behavior of single catalytic oscillators at fixed reactant pressures. In the full-scale analysis of reactions on nm-supported particles, the reactant pressures should be calculated self-consistently with the reaction kinetics. At present, due to computational limitations, the self-consistent treatment can, however, be done only by using the MF equations (see, e.g., recent simulations [57] of oscillations in CO oxidation in a continuously stirred tank reactor). The MF approach does not, however, make it possible to scrutinize the reaction kinetics on the nm scale. Under such circumstances, the MC and MF treatments are complementary. In particular, the MC results may be employed in order to understand the limits of applicability of the MF approximation.

2.6 SELECTIVITY ON THE nm SCALE

HCR involving complex polyatomic molecules usually occur via a large number of steps and result in the parallel formation of several products. In this case, the reaction rate and selectivity may easily be affected by the geometric details of nmsized catalyst particles. To simulate such reactions, one can use (with proper modifications) general approaches developed [58] to describe adsorption of complex



Figure 9 CO (*A*), O (*B*), and oxide (*C*) coverages and reaction rate (CO₂ molec. per site per MCS) as a function of time for L = 50 (a), 30 (b), 20 (c), 10 (d), 5 (e), and 3 (f). With decreasing lattice size, kinetic oscillations become more irregular. For the smallest size (L = 3), oscillations rapidly disappear due to complete poisoning of the lattice by oxygen (this is possible because O₂ adsorption is considered to occur on nn vacant sites). (Redrawn from Ref. [28].)



Figure 9 Continued.



Figure 9 Continued.



Figure 9 Continued.

molecules. The first works in this direction were published by McLeod and Gladden [59,60] (see also our review [11]).

2.7 ADSORBATE-INDUCED RESHAPING OF CRYSTALLITES

Crystallite shape transformations, due to adsorbed reactants, may affect the steadystate kinetics of catalytic reactions. Such effects can be studied phenomenologically by employing the Wulff rule [39] in order to find the optimum crystallite shape. The use of this rule implies that the crystallite reshaping time scale is shorter than the experimental time scale. The latter can be very long in practical systems.

An interesting example of application of the Wulff rule is given by Ovesen et al. [61]. They have analyzed the kinetics of methanol synthesis on nm Cu particles supported by ZnO. The generalized surface tension for the particle–substrate interface was assumed to be dependent on the reduction potential of the gas phase. The latter resulted in the dependence of the areas of the (111), (100), and (110) facets on the gas-phase concentrations (such changes were observed by using EXAFS). The total reaction rate, represented as a sum of the reaction rates on different facets, was found to be affected by the changes in particle morphology.

In our work [22], the Wulff rule was employed to analyze adsorbate-induced reshaping of crystallites during the $A + B_2$ reaction mimicking CO oxidation.

Myshlyavtsev and co-workers [62] recently tried to describe explicitly adsorbate-induced changes in the shape of catalyst particles by using the solid-on-solid (SOS) model. The results obtained are, however, somewhat artificial from the physical point of view, because the shape of particles predicted on the basis of this model has little in common with crystallites.

Generally, the possibility of a shape change of a catalyst particle, as the gasphase composition, and consequently the coverages of different species change, is both very interesting and a complicating factor-when it occurs-for interpretation of kinetic data. In an experimental situation, the largest change in adsorbate coverage (at constant temperature) occurs when the gas mixture is changed so that the system passes the rate maximum or passes over a kinetic phase transition. In both cases, there is a change in the dominant surface species. For example, for the $A + B_2$ reaction we have discussed above, there is a change from dominant B coverage to dominant A coverage as the gas-mixture ratio $P_A/(P_A + P_{B2})$ is varied from P_A below to above the rate maximum. The crystallite shapes, predicted by the Wulff rule in these situations, may be different. (An interesting open question concerns the limits of applicability of the Wulff rule in the chemically reactive systems. Originally, this rule was derived for thermodynamic equilibrium, and accordingly one could expect that it would be applicable at adsorption-desorption equilibrium. Often, the latter condition is, however, not necessary in order to use the Wulff rule.)

2.8 REACTIONS ON ULTRASMALL METAL CLUSTERS

In the previous sections, we have discussed the kinetics of HCR occurring on nmsized crystallites. The situations when the catalytic metal particles are ultrasmall are of practical importance as well. In zeolites, for example, metal particles often contain only a few atoms. Such particles called clusters can also be obtained on more conventional supports (see, e.g., recent studies of CO adsorption on Rh, Pd, and Ir clusters formed on alumina [63] and acetylene cyclotrimerization on Pd clusters on MgO(100) [64]). Reaction kinetics on clusters should be described by explicitly taking into account all possible configurations of adsorbed particles. For example, we refer to recent simulations [65] of the kinetics of a rapid $A + B_2$ reaction occurring via the Langmuir-Hinshelwood mechanism (1)-(3) on ultrasmall clusters containing a few metal atoms (see, e.g., Figure 10 showing a four-site cluster). For the infinite lattice, this reaction is bistable and accordingly may exhibit hystresis. If reaction occurs on a small cluster, the bistability and hysteresis disappear (Fig. 11). Physically, this difference in the reaction behavior results from the fact that the fluctuations of the number of adsorbed particles on a small cluster are much higher than those on the large lattice.

In general, the concepts of bistability and hysteresis are related not only to the reaction kinetics but also to the time scale of the experiment. For this reason, the lattice size corresponding to the boundary between "small" and "large" lattices depends on the time scale of the experiment as well. MC simulations [66] indicate that often the boundary size is about 5×5 . For somewhat larger lattices, one can observe the fluctuation-driven transitions between the high- and low-reactive regimes [42].



Figure 10 Seven possible types of configurations of A and B particles (filled and open circles) occurring during rapid $2A + B_2 \rightarrow 2AB$ reaction on a four-site cluster. The model used implies that A and B_2 adsorption are competitive, i.e., each site can be either vacant or occupied by A or B particles. The Langmuir–Hinshelwood step is assumed to be so fast compared to A and B_2 adsorption that there are no configurations with simultaneous adsorption of A and B particles. B particles are immobile, and A diffusion is rapid compared to the LH step. In addition, the model takes into account that strong repulsive lateral interactions between nn B particles prevent B_2 adsorption on nn sites. Specifically, B_2 adsorption is considered to occur on vacant pairs of next-nearest-neighbor sites provided that adjacent sites are not occupied by B (this detail is significant, because it prevents poisoning of the surface by B). (Redrawn from Ref. [65].)

2.9 DIFFUSION LIMITATIONS

The reaction kinetics in porous catalysts are kinetically controlled only if the reaction is sufficiently slow, while the rate of rapid reactions becomes limited by reactant diffusion via pores. Quantitatively, the role of diffusion is usually scrutinized by employing the phenomenological reaction-diffusion equations [1]. For example, in the case of the simplest first-order reaction, one has

$$\partial n/\partial t = D_{\rm ef}\Delta n - k_{\rm ef}n \tag{17}$$

where *n* is the reactant concentration, D_{ef} the effective diffusion coefficient, and $k_{ef} = k_0 N_c$ the effective reaction rate constant (k_0 is the rate constant corresponding to a single catalyst particle, and N_c is the concentration of catalyst particles). This approach is based on the assumption that the rate constant k_{ef} (or k_0) characterizes the true reaction kinetics. In other words, this constant is usually assumed to be independent of the rate of diffusion, i.e., the interplay of reaction and diffusion inside single pores is not treated explicitly. The latter aspect of the problem was


Figure 11 (a) Rate of the $A + B_2$ reaction (10⁶ AB molec. site⁻¹ S⁻¹) and (b) A and B coverages as a function of the relative A pressure for the infinite lattice (thin lines) and foursite cluster (thick lines). The results for the infinite lattice were obtained by using the conventional MF equations. The kinetics corresponding to a four-site cluster were calculated by employing the master equations, taking into account all possible configurations of adsorbed particles (as shown in the previous figure). The model parameters used in the calculations are typical for CO oxidation on noble metals at $P_{\rm CO} + P_{\rm O2} = 0.01$ bar and T = 500 K. (Redrawn from Ref. [65].)

analyzed in detail in [67,68]. Specifically, the first-order reaction was assumed to occur on the catalytically active walls of pores (the results obtained [67] justify application of the phenomenological approach). For supported catalysts, this model makes sense if the pores are so large that a multitude of catalytic particles is inside a single pore. In mesoscopic pores, this is often not the case. If, for example, the size of catalyst particles is comparable with the pore radius, a single pore will, as a rule, contain no or only one catalytic particle. Under such circumstances, the reaction rate on a single catalyst particle can be limited by diffusion inside the pore where this particle is located (see, e.g., Figure 12 reproduced from [30]). Diffusion limitations may also be significant in reactions occurring on model planar-supported catalysts. The latter case was treated in [23].

2.10 HEAT DISSIPATION ON CATALYST PARTICLES

General equations for estimation of the time scales characterizing dissipation of heat released in exothermic reactions occurring on nm-supported catalyst particles have



Figure 11 Continued.

been derived in [69,70]. The results obtained indicate that overheating a single nm particle is usually negligible. One cannot, however, exclude local overheating of a porous catalyst on the larger scale. The necessary conditions for observation of the latter phenomenon are still open for discussion.

2.11 GROWTH OF SUPPORTED nm CRYSTALLITES

Although the main subject of this review is the kinetics of HCR on nm-sized supported crystallites, it is instructive to discuss briefly the kinetics of growth (sintering) of such particles. In practical conditions, this process is usually not desirable, because it results in a decrease of the active catalyst area (one type of catalyst aging). Still it is a common phenomenon during the initial and long-term life of real catalysts. Experimental studies of this phenomenon are numerous [71–73], but the relative importances of the many factors affecting the growth are still not quite clear. In vacuum, larger crystallites usually grow at the expense of smaller ones via the Ostwald ripening scenario including 2D evaporation of metal atoms, diffusion along the support, and condensation [diffusion and collisions of crystallites may also be important but only if their size is small ($\approx 1-2$ nm)]. In atmosphere or under the chemically reactive conditions, the sintering often occurs faster. While for H₂ or N₂ this effect is usually relatively minor, oxygen-containing atmospheres may result not only in rapid sintering, occurring presumably with participation of volatile or adsorbed PtO₂ particles, but also in redispersion of crystallites.



Figure 12 (a) Schematic arrangement of a catalyst particle inside the pore of length *L*. (b) Normalized rate of the $A + B_2$ reaction as a function of the ratio of the impingement rates of *A* and B_2 for the cases when *A* diffusion limitations inside the pore are negligible (thick lines) and significant (thin lines). The model parameters employed are typical for CO oxidation on noble metals at $P_{\rm CO} + P_{\rm O2} = 0.01$ bar and T = 500 K. (Redrawn from Ref. [30].)

Phenomenologically, the sintering kinetics are usually described by employing a power law for the average linear crystallite size, $l(t) \simeq \mathscr{A} + \mathscr{B}t^x$, where x is the growth exponent, \mathscr{A} is the constant introduced to take into account that in the beginning the growth is far from the asymptotic regime, and \mathscr{B} is the constant corresponding to the asymptotic growth. Often, the exponent x is replaced by 1/n, i.e.,

$$l(t) \simeq \mathscr{A} + \mathscr{B}t^{1/n} \tag{18}$$

Experimentally, the sintering of supported nm metal particles has been studied during several decades [71–73] by using x-ray diffraction, transmission electron microscopy, and temperature-programmed desorption (the former two techniques measure the average size of particles, the latter measures surface area). Numerous data obtained in inert and reactive conditions indicate that the growth of nm catalyst particles is usually described by Eq. (18) with n = 5–11. With increasing temperature, n often decreases.

Using the conventional Lifshitz–Slyozov arguments [74,75] based on the Kelvin equation, one might expect [73,76] that the 3D crystallite growth, occurring via 2D diffusion, should follow Eq. (18) with n=4. This value, however, is much lower than observed in experiments. The appreciable difference between the theory and experiment is actually not surprising, because the applicability of the Lifshitz–Slyozov model to nm crystallites is far from obvious (e.g., the curvature of such crystallites is an ill-defined quantity).

To tackle the problem under consideration by employing MC simulations, we have adopted [77] the restricted-solid-on-solid model (RSOSM) used earlier to explore surface roughening [78,79] (this model is somewhat more realistic compared to the conventional SOS model). Applying this model to supported catalyst particles, we determine the latter as 2D arrays of columns on a square support lattice. For the nearest-neighbor columns, the heights are allowed to differ by at most 1. Lateral interaction between nearest-neighbor metal atoms forming columns is considered to be attractive, $\epsilon_1 < 0$. The binding energy of a single atom on the support is assumed to be lower compared to that on the top of a crystallite (this corresponds to the nonwetting condition). The initial disordered state was formed by successively depositing one-half monolayer of metal atoms on the support (a deposition attempt on a randomly chosen site was accepted if an arriving atom did not violate the RSOSM constraint). The algorithm for describing the system at t > 0 consisted of attempts of diffusion jumps (we used the simplest Metropolis dynamics) to nearest-neighbor and next-nearest-neighbor sites.

Typical snapshots illustrating evolution of the distribution of crystallites are shown in Figure 13. At early stages (see, e.g., Fig. 13a for $t = 10^2$ MCS), the crystallites look like bilayer islands. With increasing time, the height of crystallites becomes larger (Fig. 13b). At the latest stages, the shape of the crystallites is pyramidal (Fig. 13c).

Analyzing quantitatively the crystallite growth at temperatures of practical interest (below the roughening temperature), we have found (see, e.g., Figure 14) that it can be described by Eq. (18) with n = 7-8 (*n* is lower at higher temperatures). Despite the simplicity of the model, the results obtained are in much better agreement with numerous experimental data compared to those predicted by the Lifshitz–Slyozov theory. Thus, our simulations explicitly show that in general the latter theory is not applicable to describing the growth of nm crystallites. (Additional simulations treating this problem on the basis of more realistic models are, of course, desirable.)



Figure 13 A 40 × 60 fragment of the 200 × 200 lattice after (a) 10^2 , (b) 10^4 , and (c) 10^6 MC steps (MCS) at $T = 0.5 |\epsilon_{MM}|/k_B$. Columns with the heights h = 1, 2, 3, 4, 5, and 6 are indicated by filled circles and squares, open circles and squares, and plus and cross signs, respectively. (Redrawn from Ref. [77].)

Reaction Kinetics on NM-Supported Catalyst Particles



Figure 13 Continued.



Figure 14 Average crystallite size versus $t^{1/n}$ for $T=0.5|\epsilon_1|/k_B$ with n=8 (filled circles) and $T=0.7|\epsilon_1|/k_B$ with n=7 (open diamonds). (Redrawn from Ref. [77].)

2.12 CONCLUSION

The theoretical results presented in this review show that, due to purely kinetic factors, the kinetics of catalytic reactions occurring on nm-sized metal particles, exposing different crystalline facets, may be unique compared to those observed on poly- or single-crystal surfaces. Experimental studies focused on such factors are still rare but certainly will attract more attention in the near future.

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3

Electronic Structure and Chemisorption Properties of Supported Metal Clusters: Model Calculations

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- 3.7 The Metal-Support Interaction: Role of Oxide Defects
- 3.8 Conclusions

SUMMARY

In this chapter we review the field of electronic structure calculations on metal clusters and nano aggregates deposited on oxide surfaces. This topic can be addressed theoretically either with periodic calculations or with embedded cluster models. The two techniques are presented and discussed underlying the advantages and limitations of each approach. Once the model to represent the system is defined (periodic slab or finite cluster), possible ways of solving the Schrödinger equation are discussed. In particular, wave function based methods making use of explicit inclusion of correlation effects are compared to methods based on functionals of the

electron density (DFT). The second part then describes a series of applications, mostly based on DFT cluster model approaches. We start with a systematic presentation of the features of isolated metal atoms on regular and defect sites of simple binary oxides like MgO and SiO₂: the first can be considered as a prototype of an ionic oxide, while the second is a typical oxide with strong covalent character of the bond. The analysis is then extended to TiO_2 as an example of transition metal oxide. The role of point defects in the stabilization of supported metal clusters and in the activation of very small clusters or even metal atoms is discussed in the last part of this chapter.

3.1 INTRODUCTION

Metal-ceramic interaction is relevant in several areas of modern science such as corrosion, adhesion, microelectronic devices, photovoltaic cells, protective coating of metals, etc. [1–7]. In addition, highly dispersed metal particles supported on oxides make up an important class of heterogeneous catalysts. Oxide surfaces serve not only as inert support for the active component, but they are actually able to stabilize metal particles of a particular dispersion grade or to alter electronic and chemisorption properties of these species. Experimental findings of significant changes in the catalytic performance of supported transition metal species have stimulated a particularly high interest in the question of how the support affects the chemisorption and the catalytic properties of active sites. The complicated phenomenon of metal-support interaction comprises a variety of mechanisms, among them the direct local electronic effect of oxide surfaces on supported metal particles. Despite this considerable technological importance, very little is known about the microscopic nature of the interface between the surface of an oxide substrate, like MgO, SiO₂, Al₂O₃, TiO₂, etc., and the contact metal atoms of a supported particle or of a metallic overlayer. This lack of information is both structural and theoretical. Most of the technologically interesting materials are based on amorphous components, but there are open structural questions even for singlecrystal experiments, like the possibility of surface reconstruction, the presence of defects and dislocations, local disorder, etc. For these reasons the theoretical description of the metal-oxide interaction is especially challenging.

More recently, considerable experimental effort has been spent to better characterize the formation of metallic overlayers, emphasizing the very first stages of metal deposition [8–17]. This intense experimental activity is complemented by a rather limited number of "first-principles" theoretical studies dealing with the general problem of metal–ceramic interaction [18–28]. For adsorbed metal atoms, two types of interactions are usually assumed, chemical bonds (mainly with the surface oxygen atoms) on the one hand, or van der Waals interaction and/or weak polarization bonds with no metallization of the surface [29] on the other hand. In the initial step of forming a metallic film, metal atoms impinge on the substrate. These atoms can be reflected from the surface or they may stick to the surface, diffuse on it, and eventually re-evaporate. Condensation can occur if the flux of adsorbed atoms is larger than the flux of re-evaporated atoms, and it is clear that the strength of the bond with the surface plays an essential role in this process.

In this chapter we review the results of calculations on single metal atoms and on nano-clusters interacting with oxide substrates, in particular MgO, SiO₂, and TiO₂, and also provide a minimum theoretical background to understand the capabilities and limitations of these model calculations. We discuss the interaction of single, isolated, transition metal atoms with the sites of the MgO surface to gain a more systematic understanding of the interface bond [30,31]; we consider small metal clusters interacting with the terrace sites of MgO to better understand the early stages of metal deposition and cluster growth [32-34]. Since an important aspect of the metal-oxide interface is related to point defects where the metal growth usually occurs, some attention is given to the main defects present on the MgO surface and to their interaction with adsorbed metal atoms. We then consider the interaction of isolated metal atoms with simple models of the nondefective and of the defective silica surface [35], and we discuss the structure of small Cu clusters on this surface [36,37]. The third substrate considered is TiO₂, and we describe the adsorption properties of alkali metal atoms as well as of Cu, Ag, Pd, and Au atoms on this surface [38,39]. Finally, we consider the extent of the perturbation induced by the substrate on the electronic properties of the supported metal cluster and the changes induced by the metal-oxide interface bond on the reactivity of the supported species.

3.2 SURFACE MODELS

3.2.1 Periodic Models

The electronic structure of solids and surfaces is usually described in terms of band structure. To this end, a unit cell containing a given number of atoms is periodically repeated in three dimensions to account for the "infinite" nature of the crystalline solid, and the Schrödinger equation is solved for the atoms in the unit cell subject to periodic boundary conditions [40]. This approach can also be extended to the study of adsorbates on surfaces or of bulk defects by means of the supercell approach in which an artificial periodic structure is created where the adsorbate is translationally reproduced in correspondence to a given superlattice of the host. This procedure allows the use of efficient computer programs designed for the treatment of periodic systems and has indeed been followed by several authors to study defects using either density functional theory (DFT) and plane waves approaches [41–43] or Hartree–Fock-based (HF) methods with localized atomic orbitals [44,45].

The presence of the adsorbate in the surface unit cell, however, results in a periodic repetition of the ad-atom or molecule in the two directions of space, hence modeling high coverage. The only way to reduce the adsorbate concentration is to increase the size of the unit cell, a solution that implies a very large computational cost. Periodic calculations for supercells containing several tens of atoms are routinely done today. Even for large supercells containing ≈ 100 atoms, however, the coverage may be too large. The supercell approach is therefore based on the assumption that the adsorbates do not interact appreciably except when they are very close to each other, so that rapid convergence is achieved with increasing size of the supercell approach is feasible but less reliable because of the long-range Coulomb interaction between the adsorbed ions. Methods to include correction terms to account for these spurious interactions have been proposed [46].

3.2.2 Cluster Models

An alternative approach to the periodic band structure methods to study solids is the cluster approach [47–50]. Here one explicitly considers only a finite number of atoms to describe a part of the surface while the rest is treated in a more or less simplified way (embedding). The main conceptual difference is that in the cluster approach one uses molecular orbitals, MO, instead of delocalized bands. The description of the electronic properties is thus done in terms of local orbitals, allowing one to treat problems in solids with the typical language of chemistry, the language of orbitals. This is particularly useful when dealing with surface problems and with the reactivity of a solid surface. In fact, the interaction of gas-phase molecules with a solid surface can be described in exactly the same way as the interaction of two molecules. Of course, the cluster model is also not free from limitations. The most serious one is that the effect of the surrounding is often taken into account in a more or less approximate way, thus leading to some uncertainties in the absolute values of the computed quantities. It is also possible that some properties are described differently depending on the size of the cluster used. It is therefore necessary to check the results versus cluster size and shape. The advantages, besides a smaller computational cost, are (1) that in describing adsorbates a very low coverage is considered so that no mutual adsorbate-adsorbate interaction is present in the model and (2) that theoretical methods derived from quantum chemistry can be applied. The latter is an important advantage and should not be underestimated. In fact, in this way it is possible (1) to explicitly include correlation effects in the calculations through, for instance, a configuration interaction (CI) procedure (see below) and (2) to treat exactly the nonlocal exchange as in the Hartree–Fock formalism; in DFT, in fact, the exchange is taken into account in an approximate way through the exchangecorrelation functional. This second aspect can be particularly important for the description of magnetic molecules or radical species.

Therefore, cluster calculations represent an alternative way of describing localized bonds at surfaces as well as defects in ionic crystals. The problem is to introduce in a reasonable way the effect of the rest of the crystal. Completely different strategies can be adopted to "embed" clusters of largely covalent oxides, like SiO₂, or of very ionic oxides, like MgO. In SiO₂ and related materials the cluster dangling bonds are usually saturated by H atoms [48,50]. The saturation of the dangling bonds with H atoms is an important aspect of the embedding, but not the only one. In fact, in this way one neglects the crystalline Madelung field. While this term is less important in more covalent materials like silica, it is crucial in the description of solid surfaces with more pronounced ionic character, like that of MgO.

3.2.3 Embedding Schemes

The very ionic nature of MgO implies that the Madelung potential is explicitly included. Indeed, several properties of MgO are incorrectly described if the long-range Coulomb interactions are not taken into account [51]. A simple approach is to surround the cluster of Mg and O ions by a large array of point charges (PC) of value ± 2 to reproduce the Madelung field of the host at the central region of the cluster

[52]. However, the PCs polarize the oxide anions at the cluster border and cause an incorrect behavior of the electrostatic potential [53]. The problem can be eliminated by placing at the position of the ± 2 PCs around the cluster an effective core potential, ECP, representing the finite size of the Mg²⁺ core [54]. No basis functions are associated to the ECP [55], which accounts for the Pauli or exchange repulsion of the O^{2-} valence electrons with the surrounding. This is a simplified approach to the more rigorous ab initio model potential (AIMP) method [56,57] but is computationally simple and reliable. In the AIMP approach the grid of bare charges is replaced by a grid of AIMPs that account not only for the long-range Coulomb interaction but also for the quantum mechanical short-range requirements of exchange and orthogonality without explicitly introducing extra electrons in the model.

The addition of the ECPs to the cluster results in a better representation of the electrostatic potential and hence of the electrostatic contribution to the surface bonding. Still missing from this simplified approach is the polarization of the host crystal induced by an adsorbed species. This effect can be particularly important for charged adsorbates.

The polarization, E_{pol} , induced by a charge on the surrounding lattice can be estimated by means of the classical Born formula [58]:

$$E_{\rm pol} = -(1 - 1/\varepsilon)q^2/2R \tag{1}$$

where ε is the dielectric constant of MgO, q is the absolute value of the charge, and R is the radius of the spherical cavity where the charge is distributed. Since a certain degree of ambiguity remains in the definition of R, this correction is only qualitative. A more refined approach that has been used for the study of the ground state of oxygen vacancies (F centers) in MgO [59] makes use of the ICECAP program [60]. In this approach instead of PCs the cluster is surrounded by polarizable ions described according to the shell model [61,62]; in this way the polarization response of the host is taken into account self-consistently up to infinite distance. In the shell model an ion is represented by a point core and a shell connected by a spring to simulate its dipole polarizability. A similar method has been applied recently to the study of energy states of defect sites at the MgO surface [63]. A quantum cluster has been embedded in a finite array of PCs placed at the lattice sites. The part of the ions closest to the quantum cluster has been treated by the shell model in such a way that they interact among themselves and the quantum cluster via specific interatomic potentials. The positions of the cores and shells of the ions are optimized in response to the changes in charge density distribution within the quantum cluster to minimize the total energy of the system [63].

An alternative, more rigorous approach has been developed in recent years by Pisani and co-workers [64–66]. It is named the *perturbed cluster method* and is based on the EMBED computer program [67]. With this approach the properties of adsorbates at the surface of MgO have been studied at the HF and MP2 levels. The method relies on the knowledge of the one-electron Green function G^{f} for the unperturbed host crystal, which is obtained by means of the periodic program CRYSTAL [68,69]. A cluster (C) containing the adsorbate is defined with respect to the rest of the host (H). The molecular solution for the cluster C in the field of H is corrected self-consistently by exploiting the information contained in G^{f} in order to allow a proper coupling of the local wave function to that of the outer region.

3.3 ELECTRONIC STRUCTURE METHODS

In this section we provide a unified point of view of the different theoretical methods used in the study of electronic structure. This includes two rather different families of methods that nevertheless arise from the principles of quantum mechanics. On the one hand, one has the ab initio methods of computation of electronic wave functions and, on the other hand, one has the methods based in the modern density functional theory. In the forthcoming discussion we attempt to focus mainly on the physical significance rather than on mathematical foundation and technical aspects of computer implementation. Details of the methods outlined in this section can be found in specialized references, monographs [70], and textbooks [71].

Finally, one of the main goals of the methods of quantum chemistry is to explore potential energy surfaces and, thus, determine geometries of stable molecules or cluster models as well as of intermediates, transition-state structures, energy barriers, and thermochemical properties. This means that one does not need to compute only accurate energies but also energy gradients and second derivatives with respect to nuclear displacements. Energy derivatives are not trivial, and some methods offer special technical advantages when gradients or higher-order derivatives are to be computed. In addition, the proper interpretation of electronic spectra requires simultaneously handling several electronic states, and not only the ground state. When choosing a particular computational method, one must contemplate the problem to be solved, and in any case the choice a compromise between accuracy and feasibility.

3.3.1 Wave Function-Based Methods in Quantum Chemistry

The best attainable approximation to the wave function and energy of a system of Nelectrons is given by the full configuration interaction (FCI) approach. In the FCI method the wave function is written as an expansion of Slater determinants with the electrons distributed in the orbitals in all possible ways and the expansion coefficients given by the corresponding secular equation. Indeed, this is the exact solution (in a given finite orbital subspace) and it is independent on the N-electron basis used provided the different basis considered expand the same subspace. This is a very important property because it means that the total energy and the final wave function are independent of whether atomic or molecular orbitals are used as oneelectron basis to construct the Slater determinants. The use of atomic orbitals leads to valence bond (VB) theory [72], whereas use of molecular orbitals leads, of course, to the molecular orbital configuration interaction (MO-CI) theory [71]. In the FCI approach both theories are exactly equivalent and provide the same exact wave function although expressed in a different basis. The VB wave functions are relatively easy to interpret [73] because the different Slater determinants can be represented as resonant forms and usually only the valence space is considered within a minimal basis description. The reason for the use of such a limited space is that these VB wave functions are difficult to compute because of the use of a nonorthogonal basis set [74]. On the other hand, the MOs are usually taken as orthonormal, a choice that permits us to carry very large CI expansions and extended basis sets [75-77]. Notice that once a finite set of "2m" atomic/molecular spin orbitals is given, the dimension of the N-electron space and, hence, of the N- electron subspace, is also given. This is because for N electrons and "m" spin orbitals, m > N, the number of Slater determinants that can be constructed is

dim FCI =
$$\binom{2m}{N} \left(\begin{array}{c} \text{or, more precisely,} & \dim \text{FCI} = \binom{m}{N_{\alpha}} \binom{m}{N_{\beta}} \end{array} \right)$$
(2)

if the system contains N_{α} and N_{β} electrons with alpha and beta spin, respectively. The dimension of the FCI problem, i.e., the dimension of the secular equation or dim FCI, grows so fast that practical computations can be carried out for systems with a small number of electrons. Therefore, the FCI method is often used to calibrate more approximate methods [78].

The simplest *N*-electron wave function that can be imagined is a single Slater determinant, and the energy is computed as an expectation value. Of course, constraining the wave function to just one Slater determinant largely reduces the variational degrees of freedom of the wave function, and the energy is uniquely defined by the one-electron basis used to construct this particular Slater determinant.

$$|\Psi_0\rangle = \frac{1}{\sqrt{N!}} \det |\Phi_i \Phi_j \dots \Phi_N\rangle$$
(3)

The only variational degree of freedom concerns the orbital set, which is therefore chosen to minimize the energy expectation value with the constraint that the orbitals remain orthonormal. This leads to a set of Euler equations that in turn lead to the Hartree–Fock equations, finally giving the ϕ_k set although in an iterative way because the Hartree–Fock equations depend on the orbitals themselves. This dependency arises from the fact that the HF equations are effective one-electron eigenvalue equations

$$f\phi_i = \varepsilon_i \phi_i \tag{4}$$

where \hat{f} is the well-known one-electron Fock operator, sum of the kinetic energy, nuclear attraction energy, and the Coulomb and exchange effective potential operators. These effective potentials average interaction with the rest of electrons, which, of course, is given by the orbitals themselves. The final optimum orbitals are therefore those for which the effective average potential used to construct the Fock operator is *exactly* the same that will be obtained using the solutions of (4) and the effective potential is self-consistent. The optimum orbitals are then named self-consistent and HF is synonymous with self-consistent method. Solving Eq. (4) is not simple, especially for molecules, and in practice (4) is transformed to a matrix form by expanding the orbitals through the well-known MO-LCAO method originally designed by Roothaan [79], which leads to

$$\mathbf{FA} = \mathbf{SAE} \tag{5}$$

where A is the matrix grouping the coefficients entering in the LCAO and S is the overlap matrix appearing because the orbitals used in the LCAO are centered in different nuclei and, hence, are not orthogonal. The matrix Eq. (5) is also solved iteratively, and the whole procedure is termed the HF-SCF-LCAO method. An important remark here is that, because a variational approach is used, the HF

scheme is aimed to approximate the ground-state (of a given symmetry) wave function only.

The resolution of the Hartree–Fock equations leads to "2m" spin orbitals but only N, i.e., the occupied orbitals, are needed to construct the HF determinant (3). The remaining spin orbitals, unoccupied in HF or virtual orbitals, can be used to construct additional Slater determinants. A systematic way to do it is by substituting 1, 2,..., N, occupied spin orbitals by virtual orbitals leading to Slater determinants with 1, 2,..., N substitutions with respect to the HF determinant. The determinants thus constructed are usually referred to as single-, double-..., N excitations and, including all possible excitations, lead to the FCI wave function. Clearly, the FCI wave function is invariant with respect to the orbital set chosen to construct the Slater determinants. However, using the Hartree-Fock orbitals has technical advantages because, at least for the ground-state wave function, the Hartree-Fock determinant contribution to the FCI wave function is by far the dominant term. The fact that the electronic Hamiltonian includes up to two-electron interactions suggests that double excitations would carry the most important weight in the FCI wave function; this is indeed found to be the case. Therefore, one may design an approximate wave function in which only the reference Hartree-Fock determinant plus the double excited determinants are included. The result is called the doubly excited CI (DC1) method and is routinely used in ab initio calculations. The practical computational details involved in DCI are not simple and are not described here. Adding single excitations is important to describe some properties such as the dipole moment of CO [71]; this leads to the SDCI method. Extensions of SDCI by adding triple or quadruple excitations, SDTQCI, are also currently used although the dimension of the problem grows very rapidly.

The truncated CI methods described above are variational, and finding the energy expectation values requires the diagonalization of very large matrices. An alternative approach is to estimate the contribution of the excited determinants by using the Rayleigh-Schrödinger perturbation theory up to a given order. This is the basis of the widely used MP2, MP3, MP4,..., methods that use a particular partition, the Møller-Plesset one, of the electronic Hamiltonian and a HF wave function as zero-order starting point [80,81]. A disadvantage of perturbation theory is that the perturbation series may converge very slowly or even diverge. However, the MP(n) methods have a special advantage over the truncated CI expansions. In the DCI and related methods the relative weight of the different excitations differs from the one in the exact FCI wave function because of the normalization of the DCI wave function. This normalization effect introduces spurious terms and, as a result, the energy of N interacting molecules does not grow as N. This is the so-called size consistency problem and is inherent to all truncated CIs. On the other hand, the MP series is size-consistent order by order. Successful attempts to render truncated CI expansions size consistent have been reported recently [82]. However, the resulting methods are strongly related to the family of methods based on the cluster expansion of the wave function [83]. The coupled-cluster (CC) form of the wave function can be derived from the FCI one as in the case of the DCI method although here the terms included are not selected by the degree of excitation with respect to the HF determinant only. The additional condition is that the different terms fulfill the so-called linked cluster theorem [83]. The resulting system of equations is rather complicated and is not

usually solved by diagonalization but rather by means of nonlinear techniques and are not variational [84–86].

The truncated CI and CC methods perform rather well when used to approximate the ground-state wave function. This is because the HF determinant provides an adequate zero-order approach. However, this is not necessarily the case, especially when several excited states are to be studied. The logical extension of the truncated CI expansion is the so-called multireference CI (MRCI) approach where excitations, usually single and double, for a set of reference determinants are explicitly considered [87,88]; the method is referred to as the MR(SD)CI method. Energies and MRCI wave functions are obtained by solving the corresponding secular equation. Again the concept is quite simple, but solving the corresponding eigenvalue problem is not a simple task and the different computational approaches involve very smart ideas and specialized codes coupled to vector, parallel, or vectorparallel processors. For problems of chemical interest the dimension of the MRCI problem is so large that often a small block of Hs in the matrix form of the secular equation is diagonalized and the effect of the rest is taken up to second order by means of perturbation theory in different partitions. The reference space can be constructed by selecting either important determinants or important orbitals. The first idea is used in the CIPSI [89–91] method, whereas the second one is the basis of the CASMP2 [92] and CASPT2 [93-95] methods, where CAS stands for complete active space, the active space defined once a subset of orbitals is chosen and it is complete because a FCI is performed within this orbital space.

Except for the simplest Hartree–Fock approach, the logic of the methods that we have discussed is based on solving the secular problem in a finite subspace defined by the one-electron, orbital, basis chosen or in finding suitable approximations. In all cases the orbital set is fixed and, usually, obtained from a previous HF calculation. Then, the contribution of the different Slater determinants in the CI expansion or the cluster amplitudes in the CC methods is obtained either variationally, i.e., the different CI methods, through perturbation theory, i.e., the MP series and related methods, or by mixed approaches, i.e., the CIPSI method. Nothing prevents one from using the variational method to optimize the orbital set and the configuration contribution at the same time. This is the basis of the multiconfigurational selfconsistent field (MCSCF) methods, which are the logical extension of HF-SCF to a trial wave function made as a linear combination of Slater determinants [96]. The mathematical problem is conceptually very similar to that of the HF-SCF approach, namely finding an extreme of a function (the energy expectation value) with some constraints (orbital orthonormality). The technical problems encountered in MCSCF calculations were much more difficult to solve than those of the singledeterminant particular case. One of the problems faced by the earlier MCSCF methods was the poor convergence of the numerical process and the criteria to select the Slater determinants entering into the MCSCF wave function. The first problem was solved by introducing quadratically convergent methods [97,98] and the second one by substituting the determinant selection by an orbital selection and constructing the MCSCF wave function using the resulting CAS. The resulting MCSCF approach is known as CASSCF and has turned out to be a highly efficient method [99–101]. The CASSCF wave function is always precisely the zero-order wave function in the CASMP2 and CASPT2 methods and in CIPSI if desired. The CASSCF wave function has some special features worth mentioning. It is invariant with respect to rotations (linear combinations) among active orbitals. When the CAS contains all valence orbitals, the CASSCF wave function is equivalent to the wave function obtained by the spin-coupled valence bond method [102–104] when all resonant forms involving valence orbitals are included. Before closing this section we would like to mention that, in practice, configuration-state Functions (CSF) are commonly used instead of Slater determinants. A CSF is *simply* a linear combination of determinants with coefficients fixed so as to have an eigenfunction of \hat{S}^2 , the total square spin operator. The fixed coefficients are often obtained with the assistance of group theory [105]. This choice ensures that truncated CIs are spin eigenfunctions and reduces the dimension of the secular problem.

We end this short review on ab initio wave function-based methods by noting all of them can be applied to a cluster model, whereas only the Hartree–Fock can be extended to account for periodic symmetry [68].

3.3.2 Density Functional Theory-Based Methods in Quantum Chemistry

The Schrödinger equation provides a way to obtain the *N*-electron wave function of the system, and the approximate methods described in the previous section permit reasonable approaches to this wave function. From the approximate wave function the total energy can be obtained as an expectation value and the different density matrices, in particular the one-particle density matrix, can be obtained in a straighforward way as

$$\rho_0(\overrightarrow{x}) = N \iint (\Psi_0^*(\overrightarrow{x}_1, \overrightarrow{x}_2, \dots, \overrightarrow{x}_N) \Psi_0(\overrightarrow{x}_1, \overrightarrow{x}_2, \dots, \overrightarrow{x}_N) d_{\overrightarrow{x}_2} \dots d_{\overrightarrow{x}_N}$$
(6)

where the integration is carried out for the spin and space coordinates of all electrons but one. In 1964 Hohenberg and Kohn proved a theorem that states that the inverse of this proposal also holds [106]. They proved that the for a nondegenerate ground state the one-electron density determines (up to an arbitrary constant) the external potential and hence the electronic Hamiltonian, the ground-state energy, and the electronic wave function. They have proved that there exists a universal functional so that the total energy is a functional of the density; i.e., given a density there is a mathematical rule that permits one to obtain the exact ground-state energy. The resulting theoretical framework is now referred to as density functional theory, or simply DFT. Since the functional is unknown one may think that DFT is useless. However, Hohenber and Kohn have also proven a variational theorem stating that the ground-state energy is an extreme (a minimum) for the exact density and, later, Kohn and Sham proposed a general framework that permits the practical use of DFT. In the Kohn–Sham formalism one assumes that there is a fictious system on N noninteracting electrons experiencing the real external potential and that has exactly the same density as the real system. This reference system permits us to treat the Nelectron system as the superposition of N one-electron systems, and the corresponding N-electron wave function of the reference system will be a Slater determinant. This is important because in this way DFT permits us to handle discrete and periodic systems. Once the reference system allows obtaining a trial density, one needs to compute the energy of the real system, and here it is when a model for the unknown functional is needed. To this purpose the total energy is

written as a combination of terms, all of which depend on the one-electron density only:

$$E[\rho] = T_s[\rho] + V_{\text{ext}}[r] + V_{\text{coulomb}}[\rho] + V_{XC}[\rho]$$
(7)

the first term is the kinetic energy of the noninteracting electrons, the second term accounts for the contribution of the external potential, the third corresponds to the classical coulomb interaction of noninteracting electrons and, finally, the fourth term accounts for all the remaining effects, namely the contribution to the kinetic energy due to the fact that electrons are interacting, the exchange part due to the Fermi character of electrons, and the correlation contribution due to the fact that electron densities are correlated. Obviously, the success of DFT is strongly related to the ability to approximate E_{XC} in a sufficiently accurate way. Now, Eq. (7) plus the Hohenberg-Kohn variational theorem permit us to vary the density by varying the orbitals, which are now referred to as Kohn-Sham orbitals. In addition, the Kohn-Sham orbitals can be expressed in a given basis set as in the usual LCAO approach. When a CGTO basis is used, one has the LCGTO-DF methods [107,108]. The orbital variation must preserve the orthonormality of the orbitals in the Kohn-Sham reference system to hence maintain the number of electrons. The overall procedure is then very similar to Hartree–Fock, and the orbitals minimizing (7) while preserving orthonormality are those satisfying a one-electron eigenvalue problem such as (4), but here the one-electron operator contains the exchange and correlation effective potentials as well and indeed as local one-electron operators. Mathematically the exchange and correlation potentials are the functional derivative of the corresponding energy contributions in Eq. (7). Once $E_{XC}[\rho]$ (or more precisely $E_X[\rho]$ and $E_C[\rho]$) is known, the effective potentials are known and solving the Kohn–Sham equations is similar to solving the Hartree–Fock equation with the important difference that here one may find the exact solution if the $E_{XC}[\rho]$ is the exact one. Notice that there is no guarantee that the final electron density arises from a proper wave function of the corresponding Hilbert space through Eq. (6). This is the famous representability problem; it does not affect the practical use of DFT and is not discussed further here. The interested reader is addressed to the more specialized literature [109].

Several approaches to $E_{XC}[\rho]$ have been proposed in the last several years with increasing accuracy and predictive power. However, in the primitive version of DFT the correlation functional was ignored and the exchange part approximated following Slater's $\rho^{1/3}$ proposal, the method was known as $X\alpha$. In 1980 Vosko et al. [110] succeeded in solving the electron correlation for a homogeneous electron gas and establishing the corresponding correlation potential. The resulting method, including also the exchange part, is known today as the local density approximation (LDA) and has been successful in the description of metals, bulks, and surfaces, although it has experienced more difficulties in the description of molecules and ionic systems; for instance, LDA incorrectly predicts NiO to be a metal [111,112]. The Kohn-Sham equations were initially proposed for systems with a closed-shell electronic structure and hence suitable to study singlets. The study of open-shell systems can be carried out using a spin unrestricted formalism. In this case different spatial orbitals are used for alpha and beta spin orbitals. In the case of LDA the resulting formalism is known as the local spin density approximation (LSDA), or simply local spin density (LSD). This is similar to the well-known unrestricted Hartree–Fock (UHF) formalism and suffers from the same drawbacks when dealing with open-shell systems [71]. This is especially important when attempting to study magnetic systems with many open shells. The unrestricted Kohn–Sham determinant corresponds necessarily to a mixture of the different possible multiplets in the electronic configuration represented by the Kohn–Sham determinant.

In spite of the inherent simplifications, LDA (and LSDA) predictions on molecular geometries and vibrational frequencies are surprisingly good. However, bonding energies are much less accurate and require going beyond this level of theory. This is also the case when dealing with more difficult systems such as biradicals or more delicate properties such as magnetic coupling in binuclear complexes or ionic solids [113–115]. The DF methods that go beyond the LDA can be grossly classified in gradient corrected (GC) and hybrid methods. In the first set the explicit calculation of the $E_{XC}[\rho]$ contributions involves not only the density, ρ , but also its gradient, $\nabla \rho$. The number of GC is steadily increasing but among the ones widely used we quote the Becke exchange functional [116] (B) and the Perdew-Wang [117,118] (PW) exchange correlation functional. The latter is usually referred to as the generalized gradient approximation (GGA) and is particularly used in condensed matter and material science. Another popular gradient corrected correlation functional is the one proposed by Lee-Yang-Parr [119] based on the work of Colle and Salvetti on the correlation factor [120]. In some cases one uses B for the exchange and PW for the correlation part—this is usually referred to as BP or B for the exchange and LYP for the correlation part, giving rise to the BLYP method. The term *hybrid functionals* is used to denote a family of methods based on an idea of Becke [121]. This approach mixes DF and Fock exchange and local and GC correlation functional in a proportion that is obtained from a fit to experimental heats of adsorption for a wide set of molecules. The most popular hybrid method is B3LYP, where the number indicates that three parameters are fit to experiment. For a more detailed description about GC and hybrid methods, the reader is referred to general textbooks [122] or to more specialized literature [108,109].

Aside from the great advances in the development of new exchange-correlation functionals, the question of which functional provides the best chemical accuracy is still under discussion. In the wave function-based methods it is possible to check the accuracy of a given level of theory by systematic improvement of the basis set and of the level of treatment of electron correlation. Unfortunately, this is not completely feasible in the framework of DFT. One can improve the basis set, but there is no way to systematically improve the $E_{XC}[\rho]$. Therefore, one needs to establish the accuracy of the chosen approach by comparing several choices for $E_{XC}[\rho]$. For many systems this choice is not critical, and the use of several functionals permits one to add error bars to the computed quantities. However, in the systems of interest in the present work, namely the description of the transition metal-oxide interface, the choice of the functional has been shown [123] to be crucial. An extreme case is that of Cu adsorption on MgO: the reported adsorption energies range from a practically unbound Cu atom at the Hartree-Fock level to a moderate adsorption, 0.35-0.90 eV, at gradient corrected DF level, to strong adsorption, about 1.5 eV, using the local density approximation, LDA. Recently Ranney et al. [124] extrapolated the adhesion energy of a single copper atom on MgO from their microcalometric measures of the heat of adsorption and found a value of 0.7 eV. The comparison of this value with the computed adsorption energies of [123] indicates that, among the currently used approximations of the exchange-correlation functional, the pure DF ones seem to provide the best answer, while hybrid functionals slightly underestimate the adsorption energy.

3.4 THE MgO SUBSTRATE

3.4.1 Transition Metal Atoms on MgO(001)

Understanding the bonding mechanism of individual metal atoms with the surface of a simple oxide like MgO is an essential prerequisite for the theoretical study of more complex systems, like clusters or organometallic fragments, supported on oxide substrates. In the following we review the interaction of various transition metal (TM) atoms, Cr, Mo, W, Ni, Pd, Pt, Cu, Ag, and Au, with the oxygen anions of the MgO(001) surface. We restrict the analysis to these sites as it is known from other theoretical investigations that the Mg cations of the surface are rather unreactive. The cluster used to simulate the MgO(001) surface is O₉Mg₉ (see Figure 1 for an example of an MgO cluster), and the calculations have been performed at the DFT level using the BLYP method; i.e. Becke's exchange functional [116] and the Lee-Yang-Parr correlation functional [119]. For further details see [30].

Cu, Ag, Au

The presence of a filled d shell and a singly occupied s orbital prevents the Cu, Ag, and Au atoms ($d^{10}s^1$ atomic ground state) from easily changing their configuration during bond formation. The lowest-lying excited state, d^9s^2 , is in fact about 1.7 eV higher than the ground state for Cu and Au, and about 4 eV higher for Ag. On the other hand, Cu, Ag, and Au could, in principle, form relatively strong bonds with oxygen atoms of not completely reduced oxide surfaces by partial transfer of their outer electron to the substrate. We will see that this is the case for TiO₂; see Section 3.6.1. The ground state of the surface cluster plus adsorbate is ²A₁ for all atoms of



Figure 1 $Mg_{21}O_{20}$ cluster model of the MgO surface. The central atom in the first layer has been removed to represent an oxygen vacancy or F center. The cluster is embedded in a large array of point charges (not shown).

the triad and the adsorbed atoms retain their $nd^{10}(n+1)s^1$ atomic configuration. However, a very small mixing of the metal σ orbitals with the O $2p_{\sigma}$ orbital also occurs. All atoms are weakly bound to the surface. The dissociation energy goes in fact of 0.2–0.3 eV for Cu, Ag, and Au. The weak bonding is shown also by the very low values of the frustrated translation, perpendicular to the surface, which is characterized by a vibrational frequency of 100 cm^{-1} and smaller.

The analysis of the bonding mechanism excludes the occurrence of a charge transfer from the metal atom to the substrate. The bonding can thus be described as mainly due to the polarization of the metal electrons by the surface electric field, accompanied by a relatively modest chemical interaction. This result suggests that the oxide anions of the MgO surface are highly charged, with little tendency to ionize the adsorbed coinage atoms. The relatively weak bonding found for Cu, Ag, and Au is therefore the consequence of the large ad-atom size (due to the singly occupied valence s orbital), which determines the long surface–adsorbate distance. Ag behaves somewhat differently from Cu and Au: the bond distance is even longer than for the other two members of the triad. The smaller propensity for a metal s–d hybridization and for a mixing with the oxygen levels is most likely the reason for the weaker bonding of Ag.

Ni, Pd, Pt

The interaction of Ni, Pd, and Pt atoms with MgO is considerably more complex than that of the coinage metal atoms because of the interplay between the d^{10} , the d^9s^1 and, at least for Ni, the d^8s^2 configurations of the atoms. The interaction of free atoms with the MgO cluster gives rise to several states; the lowest triplet and singlet states, ${}^{3}B_2$ and ${}^{1}A_1$, correlate at infinite ad-atom–surface separation with MgO + M(d^9s^1) and MgO + M(d^{10}), respectively. The magnetic state, ${}^{3}B_2$, features the lowest energy for long surface-metal distances. At short distances the ${}^{1}A_1$ state becomes lower in energy, although the detailed nature of the ground state is not completely established [125]; the potential energy curve exhibits a deeper minimum and a rather high adsorption energy of about 1 eV or more, depending on the metal. The curve crossing implies that a magnetic quenching accompanies the formation of the bond. The key mechanism for the bonding is the formation of s–d hybrid orbitals, which can conveniently mix with the O $2p_{\sigma}$ orbitals; in fact, in the ${}^{1}A_1$

The bonding has a somewhat different character in Ni than for Pd and Pt. Ni exhibits a nonnegligible polarity of the bond, while Pd and Pt form a more covalent bond. This is consistent with the fact that Ni is easier to ionize. However, by no means can the bonding be viewed as a charge transfer from the metal atom to the oxide surface. The orbital analysis clearly shows a substantial mixing (hybridization) of metal *nd* and O 2p orbitals. The fact that all three atoms in the group form relatively strong bonds with the surface, compared for instance to the coinage metals, can be explained by the more pronounced tendency of the group 10 atoms to form s–d hybrid orbitals and a more direct involvement of their valence d orbitals in the bond with the oxygen. This tendency can be generally related to the s→d (or $d\rightarrow$ s) transition energies, which are considerably smaller for Ni, Pd, and Pt than for Cu, Ag, and Au.

Cr, Mo, W

The interplay between high-spin and low-spin states is of great importance in the interaction of Cr, Mo, and W atoms with MgO. These atoms have high-spin atomic ground-state configurations, $nd^5 (n+1)s^1 (^7A_1 \text{ in } C_{4y} \text{ symmetry})$; their valence d shell is therefore half-filled, and a comparison of their interaction with that of the late TM atoms is particularly instructive. For Cr the ground state of the M/MgO cluster, $^{7}A_{1}$, correctly dissociates into Cr and MgO ground states and exhibits a very shallow potential energy curve, with a minimum around 2.8 Å and a binding energy of 0.34 eV. Also for Mo the ${}^{7}A_{1}$ state is lowest in energy, with an equilibrium distance at large separation from the surface, close to 3 Å, and a binding energy of 0.33 eV. At adsorption heights below 2.2–2.3 Å, the low-spin ${}^{5}A_{1}$ state becomes energetically preferred, but again with a local energy minimum slightly higher than for the $^{7}A_{1}$ state. The two atoms, Cr and Mo, also have similar bonding properties. The bonding is largely due to polarization and dispersion, with little, if any, chemical mixing of the metal orbitals with the surface electronic states. A completely different bonding arises from the interaction of W with MgO. The interaction of W in the high-spin d⁵s¹ configuration results in a flat curve, very similar to those computed for Cr and Mo. This state, however, is not the lowest one, even for long surface-adsorbate distances. The low-spin ${}^{5}A_{1}$ state exhibits a deep minimum near 2.15 Å. In this minimum, W is bound to MgO by 0.72 eV, a chemical bond of similar strength than that calculated for the Ni triad. A population analysis has shown that in this state the d^4s^2 atomic configuration is mixed not only with the d^5s^1 state, but also with the O 2p orbitals. This is consistent with the fact that the s-d transition energy is smallest in W where the s^1d^5 and the s^2d^4 states are almost isoenergetic, in contrast to the situation for Cr and Mo. The facile s-d hybridization is actually the reason for the strong bonding of W. As for adsorbed Ni, the bond with W exhibits a considerable polar character.

In summary, the Ni triad is the only one for which strong interface bonds are formed. The adhesion energy of these atoms on top of surface oxygens is about 1 eV/atom or more. The only other metal atom considered here that exhibits a tendency to form strong bonds with the surface is W. For W, in fact, the bond strength is comparable to that of the Ni triad. The tendency to form strong bonds is connected to the fact that metal s and d orbitals hybridize and that these hybrid orbitals mix with the p orbitals of the surface oxygen. Pd is somewhat special in the Ni triad as it has the smallest binding energy. This reflects the general tendency toward a nonmonotonous behavior in many chemical properties as one moves down a TM group; in particular, second-row TM atoms often exhibit weaker interactions than the isovalent first- and third-row atoms. To some extent, this trend is observed also for the other two triads considered. The bonding of Cr, Mo, Cu, Ag, and Au to a MgO substrate, however, can be classified as weak, arising mainly from polarization and dispersion effects with only minor orbital mixing with the surface oxygen orbitals. This explains the very long bond distances found in some cases and the flat potential energy curves that result in very small force constants.

Thus, the TM atoms considered can be classified into two groups: atoms that tend to form relatively strong chemical bonds with the surface oxygen anions of MgO (Ni, Pd, Pt, and W), and atoms that interact very weakly with the surface, with adsorption energies of the order of one third of an eV or less (Cr, Mo, Cu, Ag, and Au). The interaction *does not imply a significant charge transfer from the metal to the surface*. This is an important conclusion, connected to the highly ionic nature of the MgO surface where the surface oxygen atoms have their valence almost saturated. To a first-order approximation MgO can be described in terms of classical ionic model, $Mg^{2+}-O^{2-}$. This means that the oxygen centres at the *regular surface sites of MgO(001) are almost completely reduced and are not able to oxidize adsorbed metal atoms*. This conclusion is valid for the regular surface sites, but of course adsorption phenomena at oxide surfaces can be substantially different when occurring at defect sites. In the following section we consider some of these sites and their interaction with deposited metal atoms.

3.4.2 Pd Atoms at MgO Defect Sites

Often the most important properties of materials are directly or indirectly connected to the presence of defects and in particular of point defects [126,127]. These centers determine the optical, electronic, and transport properties of the material and usually dominate the chemistry of its surface. A detailed understanding and a control at the atomistic level of the nature (and concentration) of point defects in oxides are therefore of fundamental importance also to understand the nature of the metal– oxide interface. The accurate theoretical description of the electronic structure of point defects in oxides is essential for understanding their structure-properties relationship but also for a correct description of the metal–oxide interface and of the early stages of metal deposition on oxide substrates.

MgO is a particularly well-studied oxide; the structure of the (100) singlecrystal surface is extremely flat, clean, and stoichiometric. Recent grazing incident xray scattering experiments have shown that both relaxation, $-0.56 \pm 0.4\%$, and rumpling, $1.07 \pm 0.5\%$, are extremely small [128]. However, no real crystal surface consists of only idealized terraces. A great effort has been undertaken in recent years to better characterize the MgO surface, in particular for polycrystalline or thin-film forms, which in some cases exhibit a heterogeneous surface, due to the presence of various sites. All these sites can be considered as defects. The identification and classification of the defects are of fundamental importance. In fact, the presence of appreciable concentrations of defects can change completely the chemical behavior of the surface.

The most important defects present at the surface of MgO have been recently reviewed [129,130] (Table 1 and Figure 2). These are (1) low-coordinated Mg²⁺ ions (Mg²⁺_{4c}, Mg²⁺_{3c}, etc.) with a number of neighbors lower than on the flat (100) terraces; (2) low-coordinated anions O^{2-} sites that exhibit a completely different chemistry than the corresponding five-coordinated terraces, O^{2-}_{5c} , sites [131]; (3) hydroxyl groups [132,133]; (4) oxygen vacancies (the so-called color centers or F centers); these can have different formal charges, *F* or *F*⁺ and can be located at terrace, step, and corner sites [52,134–137]; (5) cation vacancies, often classified as V_s centers [138]; (6) divacancies, created by removing a neutral MgO unit from the surface [139]; (7) impurity atoms like substitutional Ni ions, as in MgO–NiO solid solutions, or monovalent dopants like Li⁺; (8) oxygen radical anions, O⁻, which can be formed by various means on the surface, like doping the material with alkali metals ions; (9) neutral electron traps at the MgO surface, like corner Mg ions, inverse kink, etc. [63]; (10) (111) microfacets, inverse kinks and other morphological irregularities. The



Figure 2 Schematic representation of oxygen vacancies (F centers) formed at the terrace (a), edge (b), and corner (c) sites of MgO.

complexity of the problem is increased by the fact that the point defects can be located at various sites, terraces, edges, steps, and kinks [140] and that they can be isolated, occur in pairs, or even in "clusters." Furthermore, the concentration of the defects is usually low, making their detection by integral surface-sensitive spectroscopies very difficult. A microscopic view of the metal–oxide interface and a detailed analysis of the sites where the deposited metal atoms or clusters are bound become essential in order to rationalize the observed phenomena and to design new materials with known concentrations of a given type of defects.

Defect	Symbol	Schematic description
Low-coordinated cation	Mg_{nc}^{2+} (n = 3,4)	Coordinatively unsaturated cation
Low-coordinated anion	$O_{nc}^{2-m}(n=3,4)$	Coordinatively unsaturated anion
Hydroxyl group	(OH)	Proton attached to O ^{2–}
Anion vacancy	\mathbf{F}_{nc}^{m+} (m = 0,1,2; n = 3,4,5)	Missing oxygen with trapped electrons
Cation vacancy	V_{nc}^{m-} (m = 0,1,2; n = 3,4,5)	Missing cation with holes at O neighbors
Divacancy	$V_{Mg} V_{O}$	Cation and anion vacancy
Impurity atoms	$M^{n-}/O^{n-}; Mg^{2-}/X^{2-}$	Substitutional cation (M) or anion (X)
Oxygen radical	O_{nc}^{-} (n = 3,4,5)	Hole trapped at O anion
Shallow electron traps	None	Morphological sites with positive electron affinity (inverse kink, etc.)
(111) Microfacets	None	Small ensemble of Mg_{3c} or O_{3c} ions

 Table 1
 Summary of Most Important Surface Defects in MgO

At least for the case of isolated Pd atoms, a number of these sites have been explored and a classification of the defects in terms of their adhesion properties is possible [141]. We first consider the case of Pd interacting with anion sites, O_{5c} , O_{4c} , or O_{3c} . The binding energy of a Pd atom with these sites increases monotonically from $\approx 1 \text{ eV}$ (O_{5c}) to $\approx 1.5 \text{ eV}$ (O_{3c}), and consequently the distance of the Pd atoms from the surface decreases (Table 2). This is connected to the tendency of low-coordinated anions on the MgO surface to behave as stronger basic sites as the coordination number decreases [131]. However, the difference in binding energy between an O^{2-} at a terrace site or at a corner site, 0.5 eV, is not too large. Much larger binding energies have been found for other defect sites like the oxygen vacancies or F centers.

On these sites the bonding of Pd is about three times stronger than on the O anions [141–143]. There is no large difference in Pd atom adsorption energy when the F center is located at a terrace, at a step, or at a corner site; see Table 2 ($E_b \approx 3.5 \pm 0.1 \text{ eV}$). Notice that the binding energy of Pd to a F center turns out to be the same with different computational methods. In fact, cluster model studies [141] and periodic plane wave calculations [143] give almost exactly the same energy and geometry for Pd on an F_{5c} center. Thus, the Pd atoms are likely to diffuse on the surface until they become trapped at defect sites like the F centers, where the bonding is so strong that only annealing at high temperatures will induce further mobility.

The last group of defect sites considered here is that of the paramagnetic F^+ centers. These consist of a single electron trapped at the vacancy; their electronic structure has been studied in detail in polycrystalline MgO samples by EPR spectroscopy [144]. Formally these centers are positively charged as a single electron replaces an O^{2-} ion in the lattice. On these sites the binding of Pd is between that of the O_{nc} sites and of the F centers (Table 2). For instance, on F_{5c}^+ , Pd is bound by 2.10 eV, while E_b for Pd on O_{5c} is 0.96 eV and that for F_{5c} is 3.42 eV (Table 2).

Recently, the adsorption of a Pd atom on a model of a surface OH group on MgO has shown that the binding energy at this site, 2.6 eV [145], is in between that found for neutral and charged F centers, suggesting that hydroxyl groups at the oxide surface are good candidates for metal nucleation and growth [132].

Therefore, although this list is far from being complete, it provides strong evidence that in the initial phases of metal deposition the defect centers play a crucial role in stabilizing the metal atoms and in favoring nucleation and growth.

3.4.3 Metal Clusters on MgO(001)

The interaction of TM metal clusters with the surface of MgO has been studied with both cluster [32–34] and slab [146] models, but only very small clusters have been considered, containing up to 4 to 5 atoms. The metals considered are Co, Ni, Cu, Pd, and Ag, and the various isomers studied are shown in Figure 3. They can be classified into three main groups: planar or nearly planar structures with the cluster plane "parallel" to the MgO surface (Fig. 3 a–c), planar structures with the cluster plane "normal" to the surface (Fig. 3 d–f), and tetrahedral or distorted tetrahedral structures (Fig. 3 g–i). The results show that microclusters adsorbed on the regular MgO(001) surface do not necessarily tend to adhere to the surface with the largest