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Interaction of water, gases and other complexes with metal oxide surfaces

Permalink

<https://escholarship.org/uc/item/9f4162cp>

Journal

Recent Research and Development in Quantum Chemistry, 1

Author

Lester, W.A.

Publication Date

2000

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OTHER COMPLEXES WITH METAL
OXIDE SURFACE

Sunday, January 8, 2001 (VERSION 8)

C. A Taft

Centro Brasileiro de Pesquisas Físicas, Rua
Dr. Xavier Sigaud, 150, Rio de Janeiro, RJ,
cep 22290-180 Brazil

E. Longo and F. Sensato

Departamentode Química, Universidade
Federal de São Carlos, CEP 676.13565-905,
SÃO Carlos, SP, Brazil

J. B. L. Martins

Universidade de Brasilia, Instituto de
Química, Caixa Postal 04478, CEP 70919-
970 , DF, Brazil

R. Sambrano

Departamento de Matemática, Universidade
Estadual Paulista, CEP 478.17030-360,
Bauru, SP, Brazil

A L. Almeida

Universidade do Estado da Bahia-UNEB-
Campus I, Departamento de Ciências Exatas e
da Terra
Estrada das Barreiras, s/n, Narandiba, Cabula,
CEP 41195-001, Salvador-Bahia

W. A. Lester, Jr.

Chemical Sciences Division, Lawrence
Berkeley National Laboratory, and
Department of
Chemistry, University of California, Berkeley,
California 94720-1460, USA

ABSTRACT

We have reviewed the interaction of water, gases and other complexes with metal oxide surfaces. Our work can be divided into two parts. In the first part we discuss the general aspects the substrate-adsorbate interaction, i.e., historical, comparison with metal surfaces, geometrical, crystal structures, defects, basic acid-base and oxidation-reduction surface reactions, experimental techniques and theoretical-computational modeling and simulation techniques. In the

second part we discuss the results of theoretical-computational work on metal oxide surfaces, focusing on MgO, SnO₂, TiO₂ and ZnO which have been investigated by our group. We analyse adsorption and dissociation energetics, charge distribution and transfer, using both NBO and Mulliken populations, transition states, optimized geometries, lateral interactions, effects of defects, impurities, vacancies, electronic structure, Fermi level, density of states, cluster and basis sets size effects.

1. INTRODUCTION

Surface chemistry has a long and distinguished history. Today, heterogeneous catalysis serves as the basis for most petroleum and chemical technologies with substantial importance for the life sciences as well as environmental protection and has been intensively investigated with the increasingly available tools of physics, quantum chemistry and surface science. A particularly interesting and important area of catalysis and surface science is the interaction of water, gases and other complexes with transition-metal and metal oxide surfaces which can lead to the breaking and making of chemical bonds and trigger important surface-catalysed reactions [1-5]. The field of metal oxide surface science is young [6-29]. The application of ultrahigh-vacuum spectroscopic (UHV) surface science techniques to metal oxides has blossomed only within the last decade. One major problem is that of sheer complexity which is noticeable first of all with crystal structures. The most obvious difference between metals and oxides is one of conductivity. The oxides constitute a diverse

and fascinating class of materials whose properties cover the entire range from insulators, semiconductors, conductors or even superconductors. Most of the simple single-crystal oxide surfaces examined are insulators or semiconductors which has been the most important source of the lag in the growth of oxide surface science vs that of metals –causing greater difficulty in the application of charged particle spectroscopies that are the mainstays of the surface scientist's arsenal. The effects of surface charging or band-bending turns out to have been less of a challenge than expected and considerable progress is evident over the last decade in the application of a full complement of surface science techniques including LEED, XPS, AES, UPS, ISS and HREELS which may be further extended by the use of model thin-film oxides on conductive substrates although adequate control of crystallinity or surface orientation may not always be easily obtained.

The absence of metal-metal bonds in the high-valent oxides also distinguish metal oxides from metals. The metal cations are thus isolated from each other by bridging

oxygen anions resembling the metal centers in mononuclear metal complexes in solution more than they do metal atoms on an extended metal surface. The metal centers in an oxide are also not in their zerovalent state, unlike the metal centers on a bulk metal surface which leads to the suggestion that one may find analogies in the chemistry of soluble metal complexes which are often not zerovalent. Metal oxides are thus the most likely place to find strong analogies with organometallic chemistry. Oxides are also more difficult to work with than metals since simple operations such as heating, cooling, and temperature measurement in vacuum are more taxing with materials that are difficult to maintain in good thermal contact with metals. While oxides are generally higher melting than the corresponding metals, they may undergo thermal fracture or phase transformations which limit the range of materials feasible to study in single-crystal form. Due to the lower average coordination number of metal centers in oxides than in bulk metals, the correspondingly greater relative free energy cost associated with creation of coordination vacancies, as at a surface has well as the need for charge balancing at the surfaces of ionic solids there is a tendency of many oxide surfaces to undergo thermally driven rearrangement, reconstruction, or faceting. The tendency of oxide surfaces to reconstruct permits us in some cases to examine the reactivity of different surface structures using only one single-crystal sample[30-32].

In 1972 [33] a major landmark in the study of transition-metal-oxide surfaces occurred with the work of Fujishima and Honda which indicated that TiO_2 could be used as a catalytic electrode in a photoelectrolysis cell to decompose water into H_2 and O_2 , without the application of an external voltage[31]. Despite this large effort, the solar-to-hydrogen conversion efficiency

obtained with this system remained well below 1% due to the poor harvesting of sunlight by TiO_2 , whose fundamental absorption edge is in the UV region. In the mid-1980s, interest shifted to other photocatalytic application of metal oxide semiconductors, the main research thrust being placed on the photocatalytic destruction of pollutants in water in the presence of TiO_2 particles. The characterization of adsorbates on metal oxide substrates has received considerable attention since oxides play crucial roles in an extremely wide range of phenomena such as catalysis, semiconductor physics, metallurgy and microelectronics. Solid-state gas sensors for pollution monitoring and control, the environmental degradation of high-Tc superconductors; the passivation of metal surfaces against corrosion; the stability of electrode/electrolyte interfaces in fuel cells; catalysts for the partial oxidation of hydrocarbons; reduction of CO and sulfur dioxide the most dangerous components of atmospheric pollution. Metal oxide surfaces play important roles in heterogeneous catalysis and photocatalysis. Depositing metal oxides of one type on those of a second type, or metal oxide-supporting metals comprise two classes of catalytic materials used in the chemical industry to produce billions of dollars worth of chemicals each year and to remove harmful compounds from emissions (ammoxidation of alkyl aromatics, selective catalytic reduction of NOx emissions, and oxidation of dioxin and PCB emissions, epoxidation of propylene, hydrodesulfurization of crude oil, higher n-alkane dehydrogenation, olefin methathesis, oxidation of ethylene, olefin hydrogenation, polymerization of olefins, photocatalytic oxidized organic contaminants, reduction of heavy metals in industrial waste streams, conversion of toxic form of arsenic into a less toxic form. Metaloxide surface chemistry is also important in biotic

processes, surface attachment and biofilm formation, reductive and nonreductive dissolution enhanced by microbial activities, anaerobic iron oxide formation, formation of intracellular magnetite by the magnetotactic bacteria. Most commercial catalysts consist of microscopic particles of a metal supported on a high-surface area oxide. Metal oxides are also themselves catalysts for a variety of commercially important reactions [31-32].

Many key issues related to the interaction of adsorbates on metal and metal oxide surfaces may be obtained from theoretical-computational ab-initio, density functional, semiempirical, molecular simulations and hybrid quantum/classical mechanics techniques which can yield relevant information ranging from geometries to energetics to the distribution of electron density and details of catalytic chemistry that are difficult to obtain from experiment. In this review we will discuss the theoretical-computational techniques and the results obtained from investigating the interaction of water gases and other complexes on metal oxide surfaces, focusing on the MgO, ZnO, SnO₂ and TiO₂ surfaces which have been investigated by our group(6-27). We will analyse binding energies, chemisorption, dissociation, charge distribution and transfer, transition state trajectories, lateral interactions, rmping, surface reconstruction, unsaturated coordinated geometries, Fermi levels, HOMO-LUMO gaps, ionization potentials, effects of cluster size, basis sets, impurities, vacancies, terraces, kinks, steps, coordination number, acid-base and donor-acceptor interactions, diffusion, optimized geometries, comparison of semi-empirical and ab-initio methods, hydrogen bonding, and comparison with experimental results when available [1-35].

2. GEOMETRIC STRUCTURE

A knowledge of the geometric structure of metal-oxide surfaces is a necessary prerequisite to understanding their other properties. In general no one knows exactly where atoms are on the surfaces of metal oxides. However their bulk crystal structures are known very accurately. The most useful starting point in understanding the structures of metal oxides is the ionic model. The important bonding forces are those that operate between the positively charged metal cations and the negative oxide (O^{2-}) anions. Structures will be dominated by arrangements where metal ions are surrounded by oxygen and vice versa. The most important determinants of a crystal structure are the stoichiometry, or relative numbers of the different types of atoms present, and the coordination of ions, i.e., the number of ions of one type surrounding another and their geometrical arrangement. Some of the coordination geometries of metal ions that are found in oxides are tetrahedral, square planar, octahedral, distorted octahedral, distorted octahedral and cubic. Six-fold octahedral coordination and four-fold tetrahedral coordination are the most common found in the metal oxides. In the hard-sphere model the ion size is expected to be the major factor controlling the coordination geometry. However specific bonding factors related to the electron configurations of the metal ions are often involved. Elongated octahedra are often associated with a so-called Jahn-Teller distortion, driven by the arrangement of electrons in the d^4 and d^9 electron configurations. Many structures appear to be based on a close-packed or nearly close-packed array of oxide ions, with metal cations occupying interstitial sites. Both face-centered cubic (fcc) and hexagonal-close packed(hcp) arrays have octahedral and tetrahedral interstices available. Surfaces whose atomic planes are charge neutral are

referred to as non-polar surfaces, whereas surfaces that do possess a net dipole moment are called polar surfaces which are never truly stable, since the long-range electrostatic dipole fields that are present tend to drive surface reconstruction. Thermodynamics arguments dictate that all crystals must contain a certain proportion of defects in equilibrium at non-zero temperatures. Defects may be much more common at surfaces than in bulk materials, and in oxides especially they may be often responsible for many of the catalytic and other chemical properties. Many transition-metal oxides have an unusually high concentration of defects even in the bulk solids; they are associated with the possibility of variable valence or oxidation state, which is a feature of transition-metal chemistry. Bulk defects may be classified either as point defects or as extended types such as dislocations and planar defects. Elementary point defects are lattice interstitials and vacancies, impurities or dopants. Such defects normally occur in combinations which preserve the overall electroneutrality of the solid resulting in Frenkel (vacancy plus interstitial of the same type) and Schottky balancing pairs of vacancies) types of defects. Impurities may be associated with vacancies or interstitials so as to balance the charge in a similar way. There may also be an alteration in the electronic structure at sites neighboring the defect, by the occupation of impurity levels, or by changing the charge on an ion; the electrons remaining at an O^{2-} vacancy may be trapped at vacancy sites to give F^- or F^+ centers. At higher concentrations interactions can also occur between defects. No matter how perfect the bulk single crystal, how well it cleaves, or how carefully the surface is prepared, any real crystal surface will contain a large number of steps whose primary structural characteristic is the reduced ligand coordination of step-edge ions. On metal oxides step structures can become more

complicated yielding point defects in the form of kink sites. Oxide surfaces can exhibit vacancies, adatoms and substitutional/interstitial point defects, as well as reconstructions leading to surface phase boundaries and stacking faults. Defects are certainly important to the overall reactivity of metal oxide surfaces [1-29].

Some of the most studied oxide structures [1-35] are MgO, CaO, CoO, MnO, EuO NiO (rocksalt), ZnO (wurtzite), TiO_2 , SnO_2 (rutile), Cu_2O (cuprite), CuO (tenorite), $SrTiO_3$, $BaTiO_3$ (perovskite), Fe_3O_4 (spinel), LiNbO (Ilmenite), ZrO_2 , UO (fluorite), $\alpha-Al_2O_3$, Ti_2O_3 (corundum), Na_2O (antifluorite). The simplest oxide structure is the rocksalt crystal structure not only because of the bulk arrangement of the atoms, but because the surface energy is far lower for the (100) surface than for any other. The ideal geometry of the (100) rocksalt surface is unambiguous, since the bulk structure in that direction consists of layers of atomically flat planes composed of equal number of cations and anions and charge neutral; i.e., a slab of crystal having (100) faces on both side will have no net dipole moment normal to the surface, regardless of the number of planes in the slab, and the slab will have zero net charge. More structural determinations have been carried out on the surfaces of rocksalt metal oxides than on any others. The most thoroughly studied oxide is MgO, which occurs naturally as the mineral periclase. Perovskite, ABO_3 , is another relatively simple cubic oxide crystal structure. All of the (100) planes in the crystal are atomically flat, but they alternate in composition between AO and BO_2 . Both AO and BO_2 planes are non-polar since in perovskite the A cations are A^{2+} and the B cations are B^{4+} ; the O anions are considered to be O^{2-} . The rutile, tetragonal lattice is found in two of the metal oxides whose surface properties have

been most thoroughly studied, TiO_2 and SnO_2 . Three low-index faces have been studied (110), (100) and (001), whereas the (110) surface is the most stable of the low-index faces of rutile. The corundum trigonal lattice is shared by $\alpha\text{-Al}_2\text{O}_3$ oxides and several transition metal oxides. In spite of the reduced symmetry, the local ligand environment in the bulk of corundum is similar to that in the other structures discussed above whereas the cations occupy distorted octahedral sites surrounded by six O ligands. The two single crystal corundum faces that have been studied most extensively are $(10\bar{1}2)$ and (0001). In the wurtzite structure the cations are tetrahedrally coordinated with O ions in the bulk which leads to different types of surface structures than those obtained for octahedrally coordinated oxides whereas the important low-index faces are the non-polar $(10\bar{1}0)$ and $(11\bar{2}0)$ surfaces parallel to the c-axis and the polar (0001) and $(000\bar{1})$ surfaces. The spinel structure is an important class of transition-metal oxide, of formula M_3O_4 , with the cubic, although rather complicated structure. The metal cations reside in both octahedral and tetrahedral sites surrounded by O ions. Magnetite, Fe_3O_4 , is the most common mineral form, which has the inverse spinel structure with Fe^{2+} in octahedral sites, and Fe^{3+} distributed equally between octahedral and tetrahedral sites [6-35]. The predominant natural growth faces are (111) and (110)

3. EXPERIMENTAL TECHNIQUES

The geometrical arrangement of atoms and ions on the surfaces of solids is only known accurately for a relatively small number of materials. The surface-sensitive technique that has been used most extensively to determine surface geometry is low-energy electron diffraction (LEED) for X-ray scattering in bulk crystal structure determinations where a delocalized probe

that relies on the long-range order of the surface atoms to produce the constructive and destructive interference of the incident electron wave that generates a diffraction pattern. Higher-energy electrons can also be used for surface structure determination but the longer electron mean-free-path decreases the amount of surface information obtained compared to that from the bulk. This can be partly overcome by using grazing incidence and emission geometries. This is the basis of reflection high-energy electron diffraction (RHEED) where incident electrons having energies from a few keV to 100 keV are elastically diffracted at grazing incidence from surfaces. It has found widespread use in monitoring epitaxial or thin-film growth on single-crystal surfaces. Ion scattering spectroscopy (ISS) is another technique that has proven very useful in surface determinations whereas the experimental data are conceptually easier to interpret than in LEED since most ion-surface collisions involve only a single-scattering event so that kinematical theory is appropriate. Scanning tunneling microscopy (STM) and atomic force microscopy (AFM) are surface structural techniques that are truly local in that they image individual atoms and do not rely upon long-range order to produce a signal. Extended x-ray absorption fine structure (EXAFS) consists of measuring the x-ray absorption of a material as a function of x-ray energy. If the x-ray absorption process is detected via some surface-sensitive mechanism such as Auger-electron emission, surface structural information involving interatomic distances and coordination number can be obtained (SEXAFS). EXAFS-like structure has also been observed in electron-energy-loss spectra for incident-electron energies above a threshold, arising from the backscattering of the excited electron by its surroundings (EXELFS). Photoemission difference spectroscopy is a powerful method for measuring the occupied

molecular orbital structure of adsorbates and for studying adsorbate-substrate interactions. Synchrotron-based near-edge X-ray absorption fine structure (NEXAFS) spectroscopy and X-ray emission spectroscopy can also provide detailed information on the structure and bonding of adsorbates on surfaces. High-resolution electron energy loss spectroscopies (HREELS) are a powerful technique for the determination of adsorbate species through their vibrational spectra. Temperature programmed desorption (TPD) and reduction (TPR) are particularly useful for following reaction pathways on surfaces [1-2,4,30-35].

4. BASIC SURFACE REACTIONS

Because of the importance of applying principles from surface science studies, even to the extent of catalyst design, we therefore consider basic patterns of apparent mechanistic similarity in the reactions of molecules on oxide surfaces. In particular, if we can establish analogies to coordination chemistry in solution, then we can hope to short cut some of the detail required to establish surface reaction mechanisms in heterogeneous catalysts of metal oxides. The simplest division of oxide surface reaction classes is into acid-base reactions and oxidation-reduction reactions. The exposed cations and anions on oxide surfaces can be described as acid-base site pairs. The oxygen anions can act as Brønsted or Lewis base sites; the metal cations are Lewis acid sites. Hydroxyl groups bound at certain oxide surfaces may also exhibit Brønsted acidity. The Brønsted acids dissociate on a variety of oxide surfaces which results in the protonation of surface oxygen anions, and coordination of the conjugate base of the acid to surface cations. Organic molecules dissociate on various crystal planes of metal oxides. Brønsted acids can adsorb dissociatively on metal oxides and acid-base

chemistry has provided important set of standards for spectroscopic examination on oxide single crystals, just as it did for infrared spectroscopy on oxide powders in decades past. One of the key requirements for dissociation of reactants is one of coordination vacancies on the surface metal cations. Without available binding sites for the conjugate base ligands produced by Brønsted acid dissociation, this reaction is blocked. Surface base sites are also needed to abstract and to bind the protons originating from the adsorbate. Oxygen can be found in a number of coordination environments in bulk oxides, even when its formal charge is invariant. Steric arguments also suggest that the oxide anions tend to have larger ionic radii than the metal cations, thus neighboring cations in the lattice may obstruct access to oxide anions less than the anions obstruct the cations. In addition, the two moieties produced by heterolytic dissociation of Brønsted acids are of vastly different sizes. The bare proton binds to the relatively unobstructed oxide anion; the bulky organic conjugate base anion must bind to the more hindered surface metal cation. Thus the coordination environment of the surface cations may often be one of the critical surface characteristics. The low-index planes of the vast majority of oxides do, in fact, expose surface cations with at least one coordination vacancy, along with surface anions. One may thus expect such surfaces to be active for the dissociative adsorption of Brønsted acids. Regarding oxidation and reduction reactions we note that oxygen anions on metal oxide surfaces can act as Lewis as well as Brønsted bases. As such, they may oxidize adsorbed organics. We often find a straightforward analogy to the chemistry of bases in aqueous solution, as well as to the chemistry of oxygen atoms adsorbed on transition metal surfaces. The adsorption, whether dissociative or otherwise, of molecules on the surface is usually but the first in a sequence

of reactions that may be of interest. Indeed, for a catalytic process, subsequent steps which regenerate the active surface sites must occur. The menu of feasible reactions for an adsorbate, e.g. the conjugate base of a Brønsted acid, will depend not only upon its own structure, but also upon the availability of potential reaction partners. These may be fluid-phase species impinging on the surface layer, other adsorbates at the surface, or constituents of the solid surface itself [1 – 35].

5. THEORETICAL COMPUTATIONAL MODELING

Theoretical-computational calculations [1-29], based on methods which include ab-initio, density functional and semiempirical and molecular simulations techniques [1-2,4,33-45] can yield important information regarding the interaction of water, gases and other complexes on metal oxide surfaces. Topics of interest include chemisorption energetics of molecules and molecular fragments; adsorbate structure and spectra as a function of surface site; dissociative chemisorption; interaction of coadsorbed species; non-equilibrium geometries, mechanistic issues and potential surfaces; surface reactions (heats of reaction and activation energies; electronic and geometric effects of vacancies, trapping and activation). Theoretical-computational methods are needed to unravel complexities associated with surface phenomena and to provide a framework for the interpretation of experiments. Computational modeling of catalysis is an exploding field and in recognition of computational quantum chemistry's importance, Pople and Kohn received the 1998 Nobel Prize in Chemistry for their work in laying much of its groundwork. Quantum chemical calculations provide information about the smallest length scale of interest in the hierarchical approach

to modeling heterogeneous catalytic processes. Based on solution of the Schrödinger equation, results from quantum mechanics may be used to predict molecular properties ranging from geometries to energetics to the distribution of electron density and details of catalytic chemistry that are difficult to obtain from experiment. Various methods have been advanced to solve the Schrödinger equation, ranging from semiempirical methods to ab initio techniques. The basic principle that dictates the choice of a level of theory is the competition between speed and accuracy. Semiempirical methods are significantly less computationally demanding than techniques based on first principles. These methods introduce approximations to facilitate evaluation of terms introduced by electron-electron interactions and rely on parametrization against experimental data. As computational power has surged, techniques based on first principles, or ab initio methods, have been used more frequently. The ab initio methods are based on either wave function solutions to the Schrödinger equation [e.g., self-consistent field (SCF) or Hartree-Fock (HF) and self-consistent field (SCF) or Hartree-Fock (HF) and high levels of theory that treat electron correlation more exactly (such as configuration interaction (CI) or Moller-Plesset perturbation methods (MP2)), density-functional theory, or a tight-binding formalism. These methods can be further divided into two classes: 1) methods that use finite cluster of atoms to represent chemically and physically important regions of a metal oxide (cluster methods) and 2) methods that treat the solid as an infinite (periodic) system possessing translational symmetry (extended methods). Embedding schemes treat a small region of the catalyst quantum mechanically and use classical methods to incorporate long-range interactions. Slab methods use periodic

boundary conditions to treat the infinite solid. A large number of different implementations of these methods for different types of systems is available. Caution must be taken in using these approaches in modeling particular systems since they can introduce some sense of arbitrariness that makes it difficult to adapt in a general sense. Embedded cluster calculations were a first step in being able to compare theoretical results with the rich database offered by surface science experiments. To enable even more direct comparison with experimental results, *ab initio* methods that treat the infinite solid with periodic boundary conditions are being used with increasing frequency. The methods are not simply a check on available experimental data but also offer new insight into unresolved questions. Another advantage that periodic calculations offer is the ability to probe surface coverage effects and the extent of cluster edge effects. The Car-Parrinello scheme, which combines molecular dynamics with density functional calculations is another method for computing ground-state electronic properties of large and/or disordered systems(1-2,4,33-45).

Regarding atomistic simulations we note that in addition to the events at the active site, physical adsorption and diffusion can be important in a full catalytic cycle which occurs however, on a longer time- and length-scales than those currently accessible to the quantum chemical methods which have difficulty to capture accurately the often important weak van der Waals forces(1-2,4,33-42). Alternative computational simulation methods using atomistic models can be used to focus on properties such as adsorption isotherms, heats of sorption, diffusion coefficients, and activation energies for diffusion which provide short-time details of the microscopic structure and short-time motions that may be helpful in building our understanding of the systems of interest. In

general the first input to a molecular simulation is a knowledge of the chemical constitution and structure of surface and the adsorbate molecules. Other input required are a set of simple potential functions that describe the interaction energetics between adsorbates and the surface and among the adsorbate species themselves. Dispersion, repulsion and electrostatic forces are typically accounted for, as well as intramolecular forces, such as torsion angles energies for flexible sorbates. Induced dipole and other forces may also be included. The total potential energy usually approximated by a pairwise-additive potential summed over all pairs of atoms in the system. Lennard-Jones parameters for the dispersion and repulsion energies can often be taken from previous studies in the literature or estimated from empirical expressions using physical properties of the atoms such as their polarizabilities and radii. Coulombic interactions are usually modeled by placing point charges on the atoms, with the partial charge usually obtained from quantum chemical calculations. The outputs of a molecular simulation include thermodynamic properties such as adsorption isotherms and heats of sorption; dynamic properties, such as the self-diffusion coefficient and information of the molecular structure. Given the model a molecular simulation rely on statistical mechanics to generate the desired information. In general, different simulation methods are required for predicting adsorption thermodynamics and diffusion. Microkinetic modeling is an ideal framework for assembling the microscopic information provided by atomistic simulations and electronic structure calculations to obtain macroscopic predictions of physical and chemical phenomena in systems involving chemical transformations. The thrust of the approach is to write down the particular catalytic reaction mechanism of interest in terms of its most elementary steps, whereas

no rate-determining mechanistic step (RDS), which can change with reaction conditions, is assumed. Because all postulated elementary steps are included explicitly, accurate rate parameters for all of the forward and reverse reactions are needed to solve the equations comprising the model. The essence of the density functional approximation is the use in evaluating the total energy of the system of expressions for the exchange and correlation energy that are appropriate to the electron gas of uniform density. The method has the advantage that its computational requirements scale less severely with the size of the system investigated compared with Hartree-Fock methods and correlation effects are included directly, whereas HF methods must be extended to include correlation effects. The non-local exchange term also makes the HF approximation more difficult to solve than the local density functional methods. HF methods do, however, have the advantage that the approximations are more clearly defined and that there is considerable experience in establishing suitable basis sets, gained from molecular quantum chemistry [1-2,4,33-45].

Some simulations are based on an effective potential which subsumes knowledge of electronic structure into a numerical or analytical function describing the variation of the total energy of the system with the position of the nuclei. Such potentials may then be used in energy minimizations (EM) and in Monte Carlo (MC) and molecular dynamics (MD) simulations. The first of these allows an economical determination of minimum energy structures for crystals, defects, surfaces and sorbed molecules, but is limited by the static lattice approximation, the second allows ensemble averages (and their variation with temperature) to be studied; the third yields full dynamical detail albeit for a limited time period. According to the standard

quantum mechanical approach, information on temperature effects in solids can be obtained in a quasi-harmonic approximation by calculating phonon frequencies from elastic constants. If a description of the potential energy surface through classical inter-atomic potentials is available non-zero temperature effects in condensed matter may be simulated by means of molecular dynamics (MD) or Monte Carlo methods. Ab initio molecular dynamics (AIMD) is possible through the use of the Car-Parrinello (CP) method, which provides estimates of finite temperature effects through the introduction in the density-functional Hamiltonian of a fictitious temperature. The quantum Monte Carlo (QMC) method is a stochastic approach for sampling the exact wavefunction. The parameters in a trial wavefunction are optimized typically by minimizing the variance of the energy. The QMC method yields energies and other properties in excellent agreement with exact values. QMC methods offer considerable advantages over other techniques for treating electron correlation owing to the capability of including functions explicitly dependent on interparticle distances in the trial wavefunction. Among the other advantages of QMC are the comparatively mild scaling of the CPU time with the number of electrons, the inherent parallelism of the computations, and the weak dependences of the results on the basis set used in constructing the trial wavefunction used to guide the random walk. The QMC method has been demonstrated to scale better with CPU time than other methods. The use of pseudopotentials or effective core potentials (ECPs) has made possible the application of ab initio methods to large systems that would be otherwise inaccessible. ECPs have been found to yield energies of accuracy comparable with that of all-electron calculations, multireference CI and coupled cluster calculations. For this

reason, ECPs are routinely used for treating valence correlations in transition metal systems and at present make possible the application of post Hartree-Fock methods for which large bases sets are currently impractical owing to high computational demands and poor scaling. The solid can be simulated either by taking into consideration a large enough portion thereof (cluster) or by exploiting its characteristics of (quasi)periodicity. The adoption of the cluster model has the advantages that it permits us to simulate a variety of situations (bulk crystals, surfaces, defects, etc) with no substantial changes; it also allows the use of standard programs of molecular quantum chemistry. As a counterpart, different devices must be adopted to eliminate, in part at least spurious effects related to cluster termination, finite cluster size, and a wrong estimate of long range electrostatic effects). If the system is a crystal, that is, it exhibits perfect translational periodicity in three, two or one dimensions, the exploitation of this symmetry through a periodic model gives in principle enormous advantage as concerns the quality of the description and computational economy. However, it is necessary for this purpose to adopt an approximated one-electron Hamiltonian. Only under this assumption, the k-space partition of the many-electron problem (band theory) becomes possible. The selection of a given theoretical model leaves open a spectrum of technical possibilities towards the implementation of a workable computer code for crystals. The use of plane waves (PW), the universal basis set, makes most algebraic manipulations very simple. The price to pay is the high number of PWs which are necessary to describe fine details of the wavefunction, in the vicinity of nuclei. For this reason, the use of pseudo-potentials (PP) to get rid of core electrons is mandatory. The partition of space between atomic

spheres (where spherical harmonics multiplied by radial functions are used as a representative set) and interstitial regions (where PWs are used) is the characteristic feature of a whole family of techniques which have undergone continuous improvements which are specially suitable for an all-electron, very accurate description of the wave function in the proximity of the nuclei. With respect to PW, the use of suitable contracted Gaussian type orbitals (GTO) centered on nuclei permits us to describe accurately electronic distributions both in the valence and in the core region with a limited number of basis functions. Among the disadvantages associated with the choice of GTOs, there is their non-orthogonality, the need to take into account the so-called basis set superposition error, and the risk of pseudo-linear-dependence catastrophes when too diffuse functions are used. The k-partition of the periodic problem made possible by translational periodicity requires the choice of a suitable sampling set of k-points which should be as small as possible, yet representative enough to allow accurate interpolation of the reciprocal space. In crystalline quantum chemistry, we are faced with the problem of lattice sums, that is summations over one, two or three indices associated with all the cells of the crystal. The problem of the Coulomb series is present in both DFT and HF schemes, and must be treated with extreme care because the series is only conditionally convergent [1-2,4,33-45].

A state of the art analysis of the present available theoretical-computational techniques indicate that the wide range of time and length scale in heterogeneous catalysis led to the development of various modeling techniques for different questions at different scales. Quantum chemical methods are used routinely now to calculate many properties including minimum energy

configurations, electronic structures, saddle points and spectroscopic properties of diverse arrangements of atoms and even periodic structures. Atomistic modeling, using empirically derived potential interactions, can provide adsorption isotherms, heats of adsorption and diffusion coefficients from Monte Carlo and MD simulations. For systems where the diffusion times are beyond those accessible to MD, TST can be used to calculate rates of hopping between preferred sites, and these rates can be fed into more coarse-grained lattice models to predict the diffusion coefficient. Such lattice models can also be used to model combined reaction and diffusion in porous solids or on surfaces. Microkinetic modeling is used to link molecular-level information about reactants, products and reactive intermediates on heterogeneous surfaces to macroscopic kinetic observations. Mechanisms have also been postulated based on experimental and theoretical evidence whereas rate constants for each elementary step are specified from experiment, correlations or theory, and the mechanism combined with the appropriate reactor design and the full set of equations is solved to yield relative reaction rates, coverages of surface intermediates, reactant conversion, product yields and selectivities. Catalysis depends on phenomena that span a wide range of time and length scales, and this makes modeling of catalytic systems a considerable challenge. These events occur on length scales ranging from the catalytic site (10^{-10} m) up to the size of the reactor (1m). Relevant time scales may span from femtoseconds up to hours. In principle, one can predict the macroscopic phenomena of interest by solving the governing microscopic equations, namely the Schrödinger equations which can never be done feasible even with today's fastest computers. Quantum mechanical calculations can only be carried out for hundred of atoms, and the time scales

of interest are many order of magnitude beyond current capabilities. The strategy is that at different time and length scales to use different computational methods and link them together to answer questions spanning from the atomic to the macroscopic. At the most detailed level of description, electronic structure calculations are used to predict the energetics of small arrangements of atoms which can provide energetic parameters that are fed into atomistic simulations. Monte Carlo and (MD) simulations, using systems of hundreds or thousands of molecules, can be used to predict macroscopic thermodynamic and transport properties, as well as preferred molecular geometries. Preferred structures can then, in turn be analyzed in more detail with the electronic structure methods. If the time and length scales are beyond those accessible to atomistic simulation, other statistical mechanical treatments are applied. Transition-state theory (TST) can be used to predict rates of chemical reactions or rates of slow physical processes. At the longest time and length scales, continuum engineering modeling approaches such as microkinetic modeling are used to calculate properties of interest using model parameters predicted by other levels of the hierarchy [1-2,4,33-45].

6. THEORETICAL-COMPUTATIONAL STUDIES OF MgO, ZnO, SnO₂, TiO₂ AND OTHER METAL OXIDES

6.1 MgO

Magnesium based absorbents such as MgO [6,7,19-21] is environmentally important to decrease CO concentrations in exhaust gases and to reduce sulfur dioxide, the most dangerous component of atmospheric pollution. In our industrial society, sulfur SO₂ is frequently produced as a result of burning sulfur-containing impurities present in coals and fuels derived

from petroleum. In the atmosphere SO_2 contributes to air pollution and smog. It is a major contributor to acid rainfall and constitutes a serious health hazard. This toxic gas can cause severe irritation in the skin, eyes, mucous membranes and respiratory system. MgO is also a key component in modeling subsurface transport. In addition MgO is a widely used high temperature ceramic material known to be a good catalyst for many processes. For example, methanol, isomerization of *cis*-2-butene, ethanol decomposition as well as water-gas shift reactions proceed easily on a MgO catalyst. Oxidative coupling of methane has also been reported for MgO doped with K, Na, Li. Magnesium oxide crystallizes in well defined cubes or rock-salt structure in which the most stable crystallographic surface is the (100) plane. Highly dispersed fine grains may have heavily perturbed surface structure whereas MgO is an excellent model substance for highly dispersed materials which can be produced in the form of nanometer-sized particles. Unless maintained in an ultra high vacuum environment, MgO readily adsorbs water. In processes, such as the deposition of metal clusters on a MgO surface, the extent of water or hydroxyl group coverage should, in general, be taken into account because surface hydroxyl groups may influence other oxide properties such as mechanical response. Moreover, the reactivity of MgO is enhanced when doped with impurities. A number of different sites exist on the surface of severely dehydrated MgO powders and spectroscopic measurements have indicated that these differences can be attributed to the coordination of the surface ions. This picture of the surface containing ions of low coordination has been strengthened by studies of MgO smoke powders which mainly contain regular cubic particles. Transmission electron microscopy and photoluminescence spectroscopy studies have shown that appropriate pretreatments

can substantially alter the relative concentrations of the diverse types of sites. Contact with water vapor at room temperature erodes the corners and edges of the original cubic particles without attacking the bulk oxide. This leads to an increase in the number of low-coordinated surface sites of smoke powders. Despite considerable research various important questions remain unanswered regarding adsorption mechanism, saturation coverage, and the chemical nature of the adsorbate and desorption kinetics. The effect of surface morphology is also not completely understood as well as, in particular, the role of fivefold coordinate terrace sites and lower coordinate defects such as steps, kinks and vacancies. The problem is exacerbated by the use of a wide variety of MgO samples in the experimental studies, i.e., MgO smokes, powdered MgO, thin films of MgO grown on a variety of substrates, and single-crystal MgO subject to various cleaning procedures. Infrared absorption studies have indicated features which have been assigned to O-H stretching modes of free and hydrogen-bonded hydroxyl groups, respectively. There is a controversy in the literature about the chemical activity of the (100) crystallographic surface. Microgravimetry findings indicated that MgO exposed to air is completely covered by chemisorbed water, including the (100) surface. In contrast, an ultraviolet photoelectron spectroscopy (UPS) study indicated that the coverage of (100) is significantly lower than that of the (111) surface. It is argued that the high coverage of the (111) surface is due to the large number of steps in the microfaceted surface. The MgO exposed to air and baked afterwards showed irreversible damage due to an increased number of defects (6,7,19-21).

In addition to experimental work, MgO has been the subject of considerable theoretical effort. The surfaces of MgO have

been previously investigated by various theoretical *ab initio* and semiempirical methods. Early work by our group [6-7] involving Elson Longo and collaborators in 1985 investigated the mechanisms of water interaction with an MgO surface. The CNDO/2 (complete neglect of differential overlap) method was used to calculate the energies for water interaction with an MgO surface and vacancy formation. The calculations were in agreement with experimental results and showed that for low water vapor pressures water dissociates at the surface with formation of a monoprotonated vacancy and MgOH or a double vacancy of magnesium and oxygen and Mg(OH)₂. High water vapor pressures favor the formation of diprotonated magnesium vacancies and Mg(OH)₂ or Mg(OH)₂.H₂O. The CNDO/2 method was also used to analyze the interaction of CO, and isopropyl alcohol with MgO surface. The theoretical results showed that the CO₂ molecule strongly interacts with the MgO surface. This interaction can be unidentate or bidentate with a higher probability of the unidentate structure. The results are in agreement with infra-red spectroscopy and isotopic ion exchange. The isopropyl alcohol can be physically adsorbed on the surface with the possibility of the alcohol molecule decomposition forming a hydroxyl group on the MgO surface. The rate of sintering of MgO increases by increasing the partial pressures of H₂O, CO₂ and H₂, due to the sorption of these gases. The calculations are in agreement with experimental results and show that for low water vapor pressures water dissociates at the surface with formation of a monoprotonated vacancy. Investigations by other authors [19-21] and references therein) include: the interactions of water molecules at three-coordinated sites of small (MgO)₄ and (MgO)₈ clusters including full geometry optimization and correlation energy treated at the MP2 level of theory for the (MgO)₄

cluster, and predicted that H₂O chemisorbs without a barrier directly onto adjacent three-coordinated sites; periodic Hartree-Fock (PHF) theory with density-functional correlation corrections with geometry constraints to investigate adsorption and dissociation of water on MgO surfaces and concluded that hydroxylation and molecular adsorption were energetically comparable processes on step-edges, and that hydroxylation is the energetically dominant process on three-coordinated corner sites; molecular dynamics simulations and free energy calculations based on interactions described by a hybrid quantum-classical method for H₂O adsorbates on the (001) surface of MgO and compared with periodic Hartree-Fock calculations; pairwise additive potential energy expression for the water/MgO interaction to elucidate surface hopping, desorption, and intrasite rotation and flipping for the water/MgO interaction; adsorption of water on MgO surfaces with the Car-Parrinello method indicating that a H₂O molecule in the proximity of a perfect (001) surface is physisorbed, that the molecule desorbs at modest temperatures, and that on stepped surfaces the dissociation of water proceeds very rapidly; hydroxylation of MgO surfaces by dissociative adsorption of water using simulation techniques which indicated that the perfect MgO (100) surface is not amenable to hydroxylation and that adsorption is energetically favorable and preferentially occurs at low-coordinated sites; adsorption of water molecules on MgO substrates using an approach in which the molecule-substrate contributions to the potential energy are characterized by dispersion-repulsion and electrostatic interactions between molecules indicating that water molecules form planar aggregates on MgO and, at higher coverages, commensurate monolayers.

We, the authors [19-20], have investigated water adsorption and dissociation on the MgO (001) surface using both ab initio and semiempirical methods with large cluster models in order to study pure, defective (vacancies) and doped (Li, Na, K, Ca, Fe) MgO. We have analyzed the acid-base nature of our cluster model, the charge distribution of the active sites and its relationship to chemical reactivity via Mulliken (MC), natural bond order (NBO), and the electrostatic-derived method of Merz-Kollman/Singh (MKS). We have also calculated energy gaps, stretching frequencies, HOMO, binding energies, interatomic distances, and bonding angles of the pure, defective and doped MgO before and after adsorption and dissociation of water. In addition we analyzed and constructed reaction pathways, transition structures and potential energy surfaces, and calculated activation energies for water adsorption and dissociation on pure and defective MgO. The orbital eigenvalues and density of states of the MgO cluster was analyzed and compared with photoelectron spectroscopy results.

We adopted for the MgO (001) surface a nine-cube cluster model. The Mg-O distances in this model is fixed at the bulk values. The presence of impurities in a pure MgO cluster was simulated by Mg₁₅X(19)O₁₈ [X(19)=K, Li, Na, Ca, Fe and vacancy (XX) clusters where X(19) substitutes magnesium at the Mg₁₉ position. Mg₁₈ is the water adsorption site with the lowest coordination number. The Mg₁₉ site was chosen because it is the next neighbor to Mg₁₈. Ab initio calculations were performed for pure and doped MgO with Ca, Fe impurities and XX vacancies whereas semiempirical PM3 calculations were carried out for pure and MgO doped with Li, Na, K, Al impurities and XX vacancies. The ab initio calculations were done using the GAUSSIAN 94 program packages. An effective core potential (ECP)

is used for Mg and all electrons retained for oxygen. We have used the Hay and Wadt basis sets. The semiempirical calculations were performed with the PM3 method included in the MOPAC 6.0 program package. The geometrical parameters that defined the cluster were frozen during all the calculations, whereas the geometrical parameters corresponding to the adsorbed and dissociated molecules were fully optimized. The geometries of various configurations of mixed cluster models (pure, with vacancies, and with impurities) were optimized in order to determine the stationary point corresponding to the specific active site interaction of H₂O, OH and H with the MgO surfaces. The bonding sites of adsorption and dissociation investigated for each cluster were divided into four groups i) the adsorbed species interact with magnesium and oxygen atoms in the threefold coordinated site ;(ii) in the fourfold coordinated site; iii) in the fivefold coordinated site; iv) and the adsorbed species undergoes heterolytic dissociation. The strong dependence of the chemisorption and chemidissociation parameters on the coordination number of the adsorption sites (with and without defects and impurities), with stronger effects at the low coordination sites found in this study, is in agreement with experiment which indicates that active catalytic sites of MgO are low coordinated. In fact, prior to use, the MgO catalyst is typically thermally activated by heating to temperatures in excess of 1000 K in order to increase the number of surface defect sites. Furthermore, many oxide surfaces are hydroxylated and a perfect surface is difficult to be obtained experimentally. Most real surfaces contains defects, kinks, corners and edges. These sites, consisting of three or four-coordinated atoms are the sites where most chemical reactions take place. All three methods (NBO,MC,MKS) for pure MgO indicate increasing Mg site charge with

increasing coordination number. The low coordination number and small positive Mg charge will influence the reactivity of this site with Lewis base species, such as OH⁻ and H₂. Similarly, our results also indicate an increase of negative oxygen charge with increase of oxygen coordination number. We note that even with doping and vacancies we still retain the general trend of smallest positive magnesium charge and negative oxygen charges for the lowest coordination numbers. For vacancies the reduction of coordination numbers of some of the oxygen atoms close to the vacancies results in a correspondingly substantial reduction of negative charge. The fourfold coordinated oxygen atoms bonded to the impurity have different effective charges depending on the impurity. The largest changes of atomic charges occur with the introduction of vacancies. The significant variations of the HOMO observed with the introduction of impurities suggest that the introduction of impurities may influence the physical and chemical properties of our cluster model, i.e. ionization potentials, electron donation and consequently binding energies. The *ab initio* and semiempirical calculated energy gaps also indicate strong influence of the impurities which should change the reactivity of the surfaces. The *ab initio* DOS is in agreement with the experimental He II UPS spectra. Both the PM3 and *ab initio* calculations indicate a similar trend, i.e. as the adsorption site coordination number decreases, the substrate-adsorbate bond length decreases with a corresponding increase in binding energies and H-O-Mg angles. We note that since the preferential water adsorption sites are the low-coordinated corner and edge sites which represent only roughly 10% of the pure crystal, then defective, impure crystals will be better for adsorption of water on MgO surfaces, in agreement with experiment whereas our calculations suggest that water adsorption

should increase the reactivity of MgO surfaces. After water adsorption, the trend of smallest Mg charge for lowest coordination number site no longer holds. We observe larger charge transfers from water to the bare clusters with reduction of coordination number. Our PM3 and *ab initio* results indicate that most of the impurities increase the magnitude of the binding energies. Magnesium oxide surfaces doped with impurities or containing defects such as vacancies, should in general promote more water adsorption of the oxide surface. Our calculations indicate that the combined effects of doping and water adsorption can further change the energy gaps, ionization potentials and consequently modify the reactivity of the MgO surface. Regarding the preferential site for water dissociation we note that the more stable systems corresponds to the configurations where water dissociated on Mg and adjacent O with lowest coordination numbers. Our calculations indicate that the high coordination sites do not form OH groups is in agreement with experimental findings. For water dissociation the bare cluster donates charge to the atoms of the dissociated water. The charge transfer from the bare cluster upon dissociation is smaller than the charge transfer from water to the bare cluster in adsorption. For threefold magnesium coordination, charge transfer upon dissociation decreases with increasing oxygen coordination and for threefold oxygen coordination charge transfer upon dissociation increases with increasing magnesium coordination. The magnitude of the binding energies are in general larger in the corresponding configurations with impurities or vacancies as compared to the pure MgO clusters and increase with decrease of the oxygen dissociation site's coordination number. In the presence of vacancies or impurities, water dissociation strongly modifies the energy gaps, ionization

potentials and thus the surface reactivity whereas we also find that the bare cluster receives charge from the dissociated water molecule. In general we find $O_{\text{surface}}\text{-H}$ interatomic distances larger than hydroxyl (O-H) distances. The surface (Mg)- O_{hydroxyl} distance is smaller than the adsorbed surface (Mg)- O_{water} interatomic distance, both of which are in general smaller than the surface Mg-O distances. We thus find that the surface is an electron acceptor for water adsorption whereas it is an electron donor when water is dissociated. Adsorption and dissociation on low coordinated magnesium sites are more important than the equivalent interaction at low coordinated oxygen sites. There is significant charge redistribution throughout the atoms of the cluster model upon adsorption and dissociation of water. The O-H stretching frequencies can be correlated with the coordination numbers. Both two- and three-dimensional potential energy surfaces indicate an activation energy of ~ 0.4 eV at an oxygen-hydrogen separation in water of ~ 1.1 Å.

Ab initio and semiempirical (PM3) molecular orbital (MO) calculations were performed by our group [21] in order to investigate the effects of different numbers and configurations of water adsorption on three-, four-, and fivefold magnesium sites of the $(\text{MgO})_{16}$ cluster model. Our conclusions may be summarized as follows: 1) Most of the properties investigated can be correlated with the increasing number of adsorbed water molecules and with the coordination number of the Mg adsorption site. Even with increased water coverage, coordination number continues to be the preferred parameter for ascertaining the stability of the interaction. 2) When we increase the water coverage, we increase the magnitude of the total binding energy of the system, yielding a gain in stability for the higher coordination sites, however, the average $|BE|/n$ decreases.

Adsorption at the low coordinated sites stabilizes the entire adsorption process. 3) Adsorbed water geometrical parameters and surface-water interatomic distances change slightly compared to surface- OH_2 angles that define reorientation of water molecules upon adsorption. The closer the adsorbed water molecules are to each other, the greater the reorientation found. 4) Shifting of energy levels, HOMO, and LUMO as well as modification of energy gaps are observed in all the configurations investigated. As we increase the number of adsorbed water molecules, there is a tendency to reduce the band gap, raising the HOMO and lowering the LUMO. 5) There is a general tendency for the stretching frequencies to decrease with water coverage. 6) The change of Mg_i charge (ΔMg_i) is only positive for adsorption site Mg_i for one water molecule, and as we increase the number of adsorbed water molecules ΔMg_i continues to be positive only for the adsorption site Mg_i atoms. However, as we further increase the number of adsorbed molecules ΔMg_i becomes negative. Redistribution and backdonation effects appear to diminish as we increase the number of adsorbed water molecules toward saturation.

Recent DFT studies [46] of the interaction of SO_2 with MgO (100) and Cu/MgO (100) predicts no reconstruction of the clean MgO (100) surface with respect to the (100) face of bulk MgO whereas the adsorption configuration leads to a SO_3 -like species, and this is much more stable than configurations which involve bonding to only Mg sites or formation of SO_4 . On a flat MgO (100) substrate, the formation of SO_4 is not energetically viable. In the presence of appreciable concentrations of defects even unreactive molecules exhibit a rich and complex chemistry when adsorbed on MgO. A comparative study was conducted to assess the reactive adsorption of nitromethane on

the surface of MgO (100) molecules. An ab initio cluster model was used to evaluate the catalytic action of basic oxides on deprotonation. The adsorption of nitromethane and the derivatives influencing the reaction were determined and their respective energies compared (47). Hydrogen-bonded intermediate states have been observed and shown to play a decisive role in the reactivity. In a broad classification of the defect centers at the surface of MgO, one can recognize at least four major kinds of irregularities excluding extended defects and reconstructed polar surfaces. 1) Low coordinated sites which are Mg or O ions with a number of neighbors lower than on the flat (001) terraces such as the four-coordinated ions located at step and edge sites, the three-coordinated ions located at corners, kinks, etc. 2) Surface vacancies. These can be O vacancies, usually called color centers or F centers, or cation vacancies, the V centers. The vacancies can have different formal charges. The removal of a neutral atom results in a neutral F center; the removal of an O⁻ ion is an F⁺ center (paramagnetic); the removal of an O²⁻ ion is an F²⁺ center. In a similar way the removal of Mg, Mg⁺ or Mg²⁺ species result in V, V⁻ and V²⁻ defects. Since the surface ions, Mg and O, can be located at terrace, step and corner sites, the corresponding vacancies can also in principle form at five-, four- and three-coordinated centers. 3) Divacancies are closely related to the O and Mg vacancies. They are defect centers created by the thermodynamically more favorable process of removing a neutral MgO unit. 4) Impurity atoms are substitutional atoms that can lead to modify chemical centers on the surface. Recent studies [48] of the surface reactivity of MgO oxygen vacancies investigated the interaction of gas-phase molecules (O₂, CO and H₂) with oxygen vacancies (F_s centers) on the MgO (100) surface using cluster models and ab

initio wave functions indicated that the F_s centers exhibit a high reactivity towards the gas-phase molecules at variance with the regular sites of the MgO surface. The reaction proceeds through the formation of radical anions, O₂⁻ and CO⁻, via the transfer of one electron trapped in the surface cavity to the empty levels of the adsorbed molecule, and can lead to the heterolytic dissociation of the H₂ molecule. Some of the recent studies [49] and references therein) of the reactivity of F centers at the MgO surface have addressed the mechanism and the barrier for molecular dissociation at an oxygen vacancy for such systems as CH₄ and HCOOH. Another interesting case of reactivity is that of the reaction with N₂ molecules whereas EPR studies have clearly shown that exposure of a MgO surface with a high concentration of F centers these molecules results in the formation of stable or metastable radical anions. The adsorption of water molecules at defective MgO (100) surfaces was recently studied with semiempirical method MSINDO [50]. Molecular and dissociative adsorption structures and their corresponding adsorption energies were calculated.

The story [49] and references therein) of the interaction of CO with MgO surfaces began a long time ago because of the role of the CO molecule in several catalytic processes. In an early study in 1966 it was found that CO adsorbed on MgO gives rise to the formation of a paramagnetic species and to a characteristic signal in ESR experiments. The original interpretation was that two electrons are transferred from the CO 5σ orbital to the surface, while a single electron is transferred back (back-donated) from the surface to the 2π empty MO of the CO molecule reminiscent of the classical Blyholder model of the bonding mechanism of CO to metal surfaces. The first ab initio theoretical studies of CO on MgO was

reported in 1982 which indicated that CO is bound preferentially at the Mg^{2+} sites with the C-end down and that the O-down orientation is only moderately less stable. The problem was reconsidered with better basis sets and with inclusion of correlation effects in 1984 indicated that the O-down orientation of CO on Mg^{2+} sites was found to be slightly preferred. The question of the preference for C-down or O-down CO on ionic crystals has been completely elucidated in recent years. Almost 30 years of quite intensive efforts and many papers on the subject have been necessary for elucidating the key issues regarding interaction of CO with MgO surfaces. These can be summarized as follows: 1) The surface of MgO in the absence of point and extended defects is rather unreactive towards CO, at variance with the behavior of highly defective polycrystalline surfaces; 2) on a flat, defect-free (001) terrace the CO molecule binds normal to the surface with the C-end down through a largely electrostatic mechanism with little covalent contribution; 3) the strength of the bond is of the order of one tenth of an eV and the shift in the vibrational frequency is of the order of 10 cm^{-1} . 4) CO binds much more strongly and exhibits larger shifts in the C-O stretching frequency when adsorbed on the low-coordinated cations of the surface (steps, corner) where the local electric field is larger; in this respect CO represents an excellent probe to test the presence of these sites on the MgO surface. Recently [51] the liquid structure at metal-oxide-water interface within the accuracy of a three-dimensional reference interaction site model (3D-RISM) integral equation theory methodology. The spatial distributions of water oxygen and hydrogen over the surface unit cell are calculated and discussed. The 3d-RISM approach shows considerable promise as a constituent of a self-consistent description of chemical processes at a metal oxide-water interface.

6.2 ZnO

The physics of IIB-VI semiconductors has become a field of increasing technological interest. These compounds form the basis for numerous new materials and devices suitable for optoelectronics. Their polytypism and the possibility of alloying them over wide composition ranges are responsible for the observed variety of optical properties of these compound semiconductors. ZnO [8-18] is at the ionic extreme of tetrahedrally coordinated compound semiconductors whose zinc-blend or wurtzite structures lead to their classification as covalently bonded bulk materials. ZnO is thus the proto-type of tetrahedrally coordinated, ionic IIV-VI compound semiconductors which can be transformed to the characteristically ionic rocksalt (NaCl) structure by relatively modest hydrostatic pressures, and unlike most semiconductors this cubic high-pressure phase remains metastable even at zero pressure. Physically, ZnO is interesting as an example of a material where the interaction of cation d states (Zn 3d) with anion valence states (mainly O 2p) is important, and there is technological interest in ZnO for varistors, thyristors, catalysts, chemical sensors, optical coatings and use in the rubber industry where it shortens the time of vulcanisation. Also, ZnO occurs naturally as a mineral and its high-pressure phase may be geologically important as a component of the lower mantle. Its blue-UV light emitting and lasing properties have been outlined and applications in laser diodes are in progress. It is also a useful component in alcohol synthesis catalysis and gas sensing, H_2O and H_2 adsorption and dissociation, forming hydroxylated surfaces, CO oxidation in the catalytic process of methanol synthesis. Cu/ZnO is also a catalyst widely used for the synthesis of methanol ($CO+2H_2 \rightarrow CH_3OH$),

the water-gas shift reaction ($\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$), the hydrogenation of ethylene ($\text{C}_2\text{H}_4 + \text{H}_2 \rightarrow \text{C}_2\text{H}_6$), and methanol-steam reforming ($\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 3\text{H}_2$). Four low-index faces are important in the ZnO structure: the Zn-polar (0001) plane in which the Zn ions are more outwardly positioned than the O ions; the O-polar ($000\bar{1}$) plane in which the O ions more outwardly positioned than the O ions; the non-polar prismatic ($10\bar{1}0$) and ($11\bar{2}0$) planes which are atomically flat and have equal numbers of cations and anions in the surface plane. The planes can be thought of in terms of Zn-O pairs or dimers; on the ($10\bar{1}0$) face these dimers bond to ions in the plane below rather than directly to each other, while on the ($11\bar{2}0$) face they bond to each other as well as to the plane below and are arranged in zig-zag rows parallel to the c-axis. ZnO occurs naturally as the mineral zincite, although natural single crystals are rare. They cleave well along (1010). The dominant natural growth face is ($000\bar{1}$). The amount of theoretical and experimental effort devoted to ZnO may be even greater than that for MgO, partly because there is a large number of different stable crystal faces on ZnO [8 – 18].

Many theoretical [8-18] and experimental work has been done to shed light on the interaction of H_2 , H_2O , CO , CO_2 and NH_3 with the ZnO surfaces. Our group [14] has investigated the adsorption and heterolytic dissociation of H_2O and H_2 molecules on a $(\text{ZnO})_{22}$ cluster corresponding to ZnO (0001), ($000\bar{1}$), and ($10\bar{1}0$) surfaces using MNDO, AM1 and PM3 semiempirical procedures. The geometry of the adsorbed molecule has been optimized in order to analyze binding energies, charge transfer and preferential sites of interaction. Our conclusions may be summarized as follows: 1) H_2O interacts most strongly when it is

bonded to the twofold coordinated zinc atom of the cluster surface. The most stable AM1 and PM3 species has one hydrogen bonded to an oxygen atom of the ZnO cluster model. 2) Both H – O interatomic distances and H-O-H angles indicate a small deviation from the results of free H_2O . 3) The interaction of the H_2O molecule with the surface of ZnO has a charge transfer from H_2O to the surface ranging between 0.17 and 0.27 au. The neighboring atom sites are the main receptors during the process of charge transfer. 4) The results for the OH interaction on ZnO surface indicates that site I is the most stable, i.e, the bonding to the zinc atom on the borderline of the (0001) surface. 5) The interatomic distances of OH to the surface decreases relative to the interatomic distance for the H_2O interaction. Our results indicate that there is a weak bonding of hydrogen atom from OH to the oxygen surface $|d((\text{H}-\text{O})=2.00 \text{ \AA})|$, which could produce the observed O-H...O band. From a geometrical viewpoint, the Zn-H...Zn species is present in the case of the diffusion of hydrogen into the bulk. 6) The interaction of the H_2 molecule is generally weak. Our results for the nondissociative hydrogen molecule weakly interacting with the ZnO surface are in agreement with the experimental studies. The H chemisorption on the oxygen surface is more strongly bonded than is the OH chemisorption on the ZnO surface. 7) The H_2 – surface distance is less than the H_2O -surface distance. There is a charge transfer from the H_2 molecule to the surface. During the H chemisorption the oxygen transfers charge from the surface to H. 8) The O-H bond order and the force constant corresponding to the H chemisorption is less than that corresponding to the OH interaction using AM1 and PM3 methods. We suggest that the experimental bands assigned to the O-H...O species could be due to the OH species on the surface of ZnO. 9) In the heterolytic dissociation of H_2 , one hydrogen

atom becomes bonded to an exposed zinc atom as a hydride ligand at bond site I with a stretching frequency of 1623, 1818 and 2010 cm^{-1} using MNDO, AM1 and PM3 methods, respectively. The other hydrogen becomes bonded as a proton to a surface oxygen with a frequency stretching of 3703, 3502 and 3586 cm^{-1} at bond site IV for MNDO, AM1 and PM3, respectively. The experimental infrared results for the species OH and ZnH indicates a stretching frequency at 3490 and 1710 cm^{-1} respectively.

Our group [13] also investigated the interaction of a CO molecule with ZnO (0001), (000 $\bar{1}$) and (10 $\bar{1}$ 0) surfaces using the MNDO, AM1 and PM3 semiempirical procedures and a (ZnO)₂₂ cluster model. Optimization of the geometry of adsorbed CO on these surfaces was performed in order to analyze binding energies, charge transfers, stretching frequencies and force constants of the different bond sites. Our conclusions may be summarized as follows: 1) There are two main active sites I and II located between the (0001) and (10 $\bar{1}$ 0) surfaces. 2. The binding energies at bond site H range between 78 and 98 kJ mol^{-1} , whereas the experimental heat of formation is 50.2 kJ mol^{-1} . 3. The interatomic distance for the CO molecule decreases when it interacts with the cluster model bond site I. 4) There is transfer of charge from CO to the cluster model ranging between 0.17 and 0.58 au. as well as an increase of the bond order of CO in agreement with the UPS and XPS experiments. 5) A CO²⁻-like structure was found supporting the experimental results. The bond order, force constants and stretching frequencies of O_(surface)-CO are close to the free CO₂ values.

Our group [17] has also studied the CO₂ and NH₃ interaction with the ZnO surface using the AM1 method and (ZnO)₆₀ and (ZnO)₂₂ large cluster models. The adsorbed

molecules were fully optimized. The H₂/CO/CO₂ mixture plays an important role in the synthesis of methanol. However, CO₂ interaction is known to inhibit the CO interaction for methanol synthesis, protecting the surface against complete reduction or formate formation, but may also be used to promote the methanol synthesis on the Cu/ZnO catalyst. The NH₃ interaction is important to connect the surface acidic activity. The CO interaction is complex, and the NH₃ interaction could help to understand the coadsorption, since the Lewis basis NH₃ is known to adsorb physically and chemically on the ZnO surfaces bonding nitrogen to the unsaturated zinc cation. The bond sites were divided into three models (i) Type I parallel to the (10 $\bar{1}$ 0) surface; type II parallel to the (0001) surface; and (iii) bridging type V. Type C site has the lowest distance (OCO-Zn) between oxygen of CO₂ and the zinc site. Sites 2C and 3C zinc sites have coordination numbers two and three, respectively. Our conclusions are as follows: 1) We suggest that as the CO₂ interaction becomes stronger than the CO interaction, it could partially inhibit the methanol synthesis. 2) Simplified geometric models were proposed for the bridging type (10 $\bar{1}$ 0) surface from the ultraviolet photoelectron spectra results. This bridging type surface forms a [-Zn-CO₂] species in agreement with the experimental results and yield the largest change of HOMO and gap (HOMO-LUMO) and Mulliken charge. 3) The linear species III (perpendicular to the (0001) surface has a stretching frequency of 2565 cm^{-1} and a bending of 530 cm^{-1} , while the experimental values for the linear species is 2358 and 638 cm^{-1} , for stretching and bending frequencies, respectively, and the experimental free CO₂ molecule has the smallest stretching frequency at 2349 and 1333 cm^{-1} and a larger bending frequency at 667 cm^{-1} . 4) The adsorption on the 2C site has a BE between the range 118 and 157 kJ/mol , while the

adsorption on 3C site is in the range 27 to 30 kJ/mol in agreement with the experimental heat of adsorption of 118 kcal/mol. 5. The formation of $-\text{NH}_2$ yields the largest change of DOS in relation to the bare cluster model.

We [18] have also investigated the effects of lateral interactions for CO and H_2 adsorbed on large $(\text{ZnO})_{60}$ cluster models using the AM1 semi-empirical method whereas the geometric parameters of the adsorbed molecules were fully optimized. We arrived at the following conclusions: 1) A dependence of the BE on CO-CO distance for CO adsorption. 2) For CO adsorption the DOS band between -10 to -12 eV is in agreement with the experimental DOS band between -3 to -16 eV. 3) At the zinc three fold coordinated site the CO molecule are vertical above the surface and parallel to each other. 4) The BE/n decreases as the number of adsorbed CO and H_2 molecules increase. Ab initio SCF studies [52] of possible reaction pathways for the dissociation of S_2 on ZnO (0001)-Zn and Zn (10 $\bar{1}$ 0) surfaces indicated a complex adsorption in which S_2 is bridge bonded to two adjacent Zn atoms (Zn-S-S-Zn) which is probably the precursor state for the dissociation for the molecule. The presence of Cu atoms enhances the reactivity towards S_2 . Density functional theory coupled to the molecular cluster approach was used to investigate [53] the chemisorption of simple Brønsted acids (H_2O , H_2S and HCN) on ZnO (0001) polar surface. The strength of this interaction follows the order $\text{OH}^- = \text{CN}^- > \text{SH}^-$. Adsorption of formic acid (HCOOH) on ZnO (10 $\bar{1}$ 0) surfaces was investigated [54] by means of quantum-chemical ab initio periodic Hartree-Fock calculations. It was found that a tilted bridging geometry represents the most stable adsorption mode, with an adsorption energy of 52.4 kcal/mol. The coadsorption of heavy water and some aromatic molecules was studied [55] on zinc

oxide surfaces. The adsorption of benzene, toluene and α -trifluorotoluene interfered with water while the adsorption of phenol and the epoxy model compounds was affected by water.

6.3 SnO_2

Two of the metal oxides [22-29] whose surface properties have been most thoroughly studied, TiO_2 and SnO_2 , have the tetragonal rutile lattice. Three low-index faces have been studied: (110), (100) and (001). The (110) surface is the most stable of the low-index faces of rutile. Casserite, the mineral form of SnO_2 , cleaves less well along (110) than it does along (100), although neither cleave is of very high quality. Natural growth faces are also mainly (110) and (100). Although SnO_2 has the same rutile structure as TiO_2 , the differences in electronic structure result in a weaker bonding of O ions to the surface which becomes manifest in the different structures that can exist on the SnO_2 (110) surface on which the bridging O ions can be easily be removed and replaced, depending upon surface treatment. Stannic oxide in its pure form, is an n-type wide-band gap semiconductor. Its electrical conduction derives from the variable valence on the Sn atomic center, which creates point defects (native and foreign atoms) that can act as both donors and acceptors. Much of the interest in SnO_2 stems from its value in gas-sensing applications. In these applications, oxidation and reduction reactions at the surfaces or reduced SnO_2 leads to changes in conductivity. Metal oxides such as ZnO, SnO_2 and TiO_2 , are materials with varistor properties that are used as semiconductor devices which present high nonlinearity between the current density and electric field, thus being suitable for transient voltage suppression. Most of the chemistry of these oxides is due to the presence of highly reactive defective sites such as cation or

anion vacancies and/or a doping processes by substitution of metal cations. As most of the surfaces studied experimentally they contain defects resulting from preparation conditions or from ionic or electronic bombardment, one is led, after the theoretical study of ideal surfaces to consider the case of surfaces containing defects. Once the vacancies are formed, their electronic nature can be changed by adding or removing electrons. The electronic behavior is a key concept for understanding the operation. The interaction of gas-phase molecules with the various sites of SnO_2 is of growing importance in surface science with a great impulse coming from the possibility of growing thin oxide films on metal substrates and of using electrons spectroscopies in UHV to characterize the surface species. SnO_2 films have been used as resistors, transparent electrodes, sensors, and as transmissive electrochromic devices. Tin dioxide is also of particular interest because of its wide practical application for the detection of dangerous or inflammable gases and organic compounds. It is well known that tin oxide changes its conductivity when interacting with molecules in the gas phase. The catalytic importance for the selective oxidation of methane to C_1 -oxygenates made anionic oxygen species on SnO_2 the subject of much investigation with the aim of developing a one-step reaction at a lower temperature and pressure than current commercial processes, which would benefit the petrochemical industry and the environment.

We [10] have investigated the molecular hydrogen interaction with SnO_2 (110) surfaces using MNDO, AM1 and PM3 semiempirical methods. We have built and optimized nine different cluster models for the SnO_2 (110) surface. These models were designed to reproduce the possible active sites on the (110) surface of the crystal and can be classified into three categories. In

the first group, the cluster grows along the crystal c-axis direction, increasing from Sn_3O_6 to $\text{Sn}_{15}\text{O}_{30}$, with the Sn atoms in the same plane as the Sn_3O_6 cluster (Model I, II, III AND IV). In the second group, two units of SnO_2 are added in the same plane to model I to obtain Sn_5O_{10} model V. By adding two units of SnO_2 in the same plane to model V we obtain the Sn_7O_{14} model VI. For the third group, two SnO_2 units are added to model I in a perpendicular plane to produce model VII. The Sn_7O_{14} model VIII is obtained by adding four units of SnO_2 to model I in different directions (a and c-axis). From the arrangement of VI, another shell is built to produce $\text{Sn}_{15}\text{O}_{30}$ model IX. The geometries of these clusters were optimized and the dependence of geometric and electronic properties upon cluster size was investigated. The geometric parameters for the cluster model $\text{Sn}_{15}\text{O}_{30}$ indicates a slight deviation from the experimental results whereas its energy gap of 3.76 eV is in close agreement with the experimental value. The interaction between H_2 and the (110) surface was also investigated in order to analyse the gas-solid adsorption process on the surface of the hydrogen sensor SnO_2 . The H_2 interaction energy with the tin oxide surface is smaller than the corresponding interaction energy of the dissociative process. Our conclusions may be summarized as follows: 1) In order to improve description of the SnO_2 surface it is not enough to include a large number of SnO_2 units which is shown by the first group of models. It is also necessary to represent the Sn environment, as shown by $\text{Sn}_{15}\text{O}_{30}$ model IX. 2) The energy gap is dependent on the size of the cluster model. 3) Our study on different molecular hydrogen interactions with the SnO_2 surface using model IX shows that the AM1 method presents intermediate values for the calculated interaction energy, and the PM3 method gives the smallest values. 4) The results obtained for different decomposition processes suggest an

increase in the bare SnO_2 charge. The Sn atom acquires most of this negative charge, which is coincidental with the experimental increase of conductivity for the hydrogen interaction.

We [27] have also investigated the adsorption of CH_3OH (methanol) on SnO_2 (110) surface. The analysis was performed by means of the MNDO method and the clusters Sn_3O_6 and Sn_5O_{10} were used as surface models. The systematic increase of methanol molecules adsorbed on Sn_3O_6 leads to a steady lowering of the gas-surface interaction energy, except for the addition of two adsorbed molecules where a destabilization is apparent. This trend is not observed for Sn_5O_{10} used as surface models. The systematic increase of methanol molecules adsorbed on Sn_3O_6 leads to a steady lowering of the gas-surface interaction energy, except for the addition of two adsorbed molecules where a destabilization is apparent. This trend is not observed for Sn_5O_{10} where the model predicts lower interaction energies as the number of methanol molecules increases. In both cases a charge transfer towards the surface is induced which is consistent with the experimentally known increase of electronic conductivity of SnO_2 upon adsorption of methanol.

We [24] have also made a theoretical study of lithium ion interaction with tin oxide. Lithium insertion in metal oxides is a process of interest for many electrochemical applications, including rechargeable batteries and electrochromic displays. Electrochemical insertion processes modify the bulk properties of the host materials. We have used semiempirical MNDO calculations to calculate the interaction between Li^+ and $(\text{SnO}_2)_{15}$ clusters. The geometry minimization of the bare cluster model was done by maintaining the symmetry of the

crystal. The geometry optimization of the interaction between the lithium ions and the oxidized SnO_2 (110) surface which is described as an ideal surface which exposes five-coordinate Sn^{4+} cations in the second atomic layer is composed of two-coordinate O^{2-} and the presence of mono-coordinate O^{2-} is also considered. Li-O interatomic distances obtained in our calculations are in good agreement with the experimental results. Our results indicate that Li^+ adsorbs preferentially on mono-coordinate oxygen type sites. The higher energy barrier to intercalation suggests that the ion remains adsorbed at the oxide surface, but the presence of oxygen decreases this barrier favouring the Li^+ intercalation. Stable multi-coordinate bonds between the lithium and oxygen at the surface were determined which are probably associated with the characteristic electrochemical behaviour of these materials.

We [25] have also made a theoretical analysis of the energy levels induced by oxygen vacancies and the doping process (Co, Cu and Zn) on SnO_2 (110) surface models. We have used density functional calculations at the B3LYP level to study the surface oxygen vacancies and the doping process of Co, Cu and Zn on SnO_2 (110) surface models. Large clusters, based on $(\text{SnO}_2)_{15}$ models, were selected to simulate the oxidized $(\text{Sn}_{15}\text{O}_{30})$ half reduced $(\text{Sn}_{15}\text{O}_{29})$ and the reduced $(\text{Sn}_{15}\text{O}_{28})$ surfaces. The doping process was considered on the reduced surfaces. The results are analyzed and discussed based on our calculation of the energy levels along the bulk band gap region, determined by a projection of the mono-electron level structure on to the atomic basis set and the density of states. The results of our work is summarized as follow i) The creation of oxygen vacancies on going from oxidized, $\text{Sn}_{15}\text{O}_{30}$, to reduced, $\text{Sn}_{15}\text{O}_{28}$, surfaces, generates electronic states

associated to the 5s/5p orbitals of fourfold/fivefold Sn and 2p orbitals in plane O along the band gap region. The Co doping process also creates intermediate levels along the band gap, corresponding to the Cu orbitals. However, the substitution of Sn by Cu and Zn contributes only modestly to the corresponding 3d orbitals ii) The creation of one and two oxygen vacancies on an oxidized surface requires 3.0 and 3.9 eV, respectively, iv) CO doping is an exothermic process, while Cu and Zn doping process correspond to endothermic reactions iv) 3d orbitals resulting from doping process present a more favorable overlap with the 2p orbitals of O centers in the CO than in the Cu or Zn cases. These electronic states are located more closely, in energy along the valence band.

We [27] have also made an MNDO theoretical study of ethanol decomposition process on SnO₂ surfaces. A (SnO₂)₇ model has been selected to represent the surface. The decomposition process has been monitored by selection of a hydrogen- α -carbon distance of the ethanol molecule as reaction coordinate. This minimum energy profile shows a maximum of 86 kJ mol⁻¹, and in the transition state there is a transfer of hydrogen- α -carbon to the SnO₂ surface. There is also the interaction between the alcohol hydroxyls and the oxygens of the oxide.

First-principles calculations based on density functional theory and the pseudopotential method have been used to investigate [56] the energetics of H₂O adsorption on the (110) surface of TiO₂ and SnO₂. Full relaxation of all atomic positions is performed on slab systems with periodic boundary conditions, and cases of full and half coverage are studied. Both molecular and dissociative (H₂O \rightarrow OH + H⁺) adsorption are treated, and allowance is made

for relaxation of the adsorbed species to unsymmetrical configurations. For both materials in the full coverage regime molecular and dissociative adsorption are energetically favorable. However, dissociative adsorption has substantially greater adsorption energy. Investigation of a possible reaction path for the surface dissociation of water shows the absence of any energy barrier. There is an increase of adsorption energy in the half-coverage regime, which indicates the existence of an effective repulsive interaction between adsorbed species and suggests that the most stable adsorption configurations belong to the low coverage limit. Calculated valence band DOS spectra for molecular and dissociative adsorption geometries show structures similar to these of free H₂O and OH⁻ molecules. Bonding to the surface introduces small shifts and broadening of peaks in the region of the surface valence band. Recently [57] first-principles calculations were used to understand water adsorption on the SnO₂ (110) surface. Particular attention was paid to the roles played by surface geometry and inter-adsorbate interactions. Molecular water is only stable on the SnO₂ surface when bound to a neighboring OH group and that the results favour dissociative adsorption on SnO₂ at monolayer coverage.

Recently the adsorption properties of CO molecules on the SnO₂(110) surface have been investigated [58] by means of quantum-mechanical calculations. The oxide surface has been represented by clusters of ions embedded in point charges or by periodic slabs of various thickness. The methods used to compute adsorption energies, geometries and vibrational modes are Hartree Fock and density functional theory. Coverage and surface relaxation effects have been explicitly considered. The bonding and vibrations of adsorbed CO have been analyzed by decomposing the

interaction energy into the sum of various contributions. This analysis shows that the interaction of CO with the five-coordinated Sn ions of the surface has a large electrostatic character reinforced by a substantial donation of charge from CO to the cation. The CO adsorption is rather weak; the adsorption energy is accompanied by a large shift of the vibrational frequency towards higher values. Recently first-principles calculations [59] based on LDA-SCF to study changes in the electronic and atomic structures of the SnO₂ (110) surface as a result of oxygen exchange between the lattice and the ambient gas. The function relating the changes at the surface to the changes in the conductivity of a ceramic microstructure is also described by an example. Recently ab initio calculations [60] using density functional theory within the generalized gradient approximation was performed for the interaction of oxygen with a reduced SnO₂ (110) surface. Two species of chemisorbed O₂ as found that can be described as a peroxo (O₂²⁻) species for side-on type adsorption and a superoxo (O₂⁻) species for end-on type adsorption of the basis of their geometries and vibrational frequencies. They also found a low dissociation barrier of 2.0 kcal/mol for the peroxo species and high migration of barriers of ~ 13-18 kcal/mol for an oxygen atom produced by dissociation of O₂ on the reduced SnO₂ surface. An analysis of the electronic density of states indicates that an adsorbed oxygen atom coupled with the nearest-neighboring bridging oxygen vacant site is an O⁻ species that displays catalytic activity at the surface. Recently a theoretical analysis [61] based on the Hartree-Fock pseudopotential method and a density-functional theory calculation using a hybrid combination of general gradient approximation with pseudopotential procedure was carried out to study the adsorption and dissociation of methanol on the stoichiometric SnO₂ (110) surface. In the

high-coverage limit the dissociation of the methanol molecule via the heterolytic cleavage of the C-O bond is favoured. At lower coverage this channel and the molecularly adsorbed methanol present similar adsorption energies. Recent [62] plane wave (PW) pseudo-potential calculations suggest that neutral, molecular oxygen dissociates exothermically at bridging oxygen vacancies on the SnO₂ (110) surface supporting recent experimental data. Ab initio calculations [63] for the interaction of oxygen with a reduced SnO₂ (110) surface indicated a peroxo species for side-on type adsorption and a superoxo species for end-on type adsorption. An adsorbed oxygen atom coupled with the nearest-neighboring bridging oxygen vacant site is an O⁻ species that displays catalytic activity on the surface. The processes of SO₂ and CO₂ chemisorption [64] at the tin dioxide surface in the presence of oxygen and water were modeled by the MNDO method in the cluster approximation. Geometrical parameters, charge densities, and thermal-desorption properties of surface complexes that formed as a result of the chemisorption of these gases at the perfect and reconstructed surfaces were calculated. The chemisorption complexes that incorporate the peroxide fragment are the most stable complexes.

6.4 TiO₂

TiO₂ has the tetragonal rutile lattice which occurs naturally in pure form as the mineral rutile, which exhibits predominantly (110) natural growth faces, although (011) and (010) are also common. Two more complicated polymorphs of TiO₂, anatase and brookite, also exist in nature. Cleavage in the mineral form is preferentially along (110), although not of high quality. The (110) surface of single-crystal TiO₂ has been thoroughly investigated. On the TiO₂ (110) surface, the rows of bridging O ions are

tightly bound, and the removal of bridging O ion results in drastic changes in surface electronic structure. The interest in titanium oxides arises largely from the use of these materials in a wide range of industries including paints, plastics, paper, coatings, cosmetics, ceramics, electronics and even food. Rutile is an important rock-forming mineral and the most abundant TiO_2 polymorph in nature. In addition, most crystal-growth techniques basically yield titanium dioxide in the rutile phase. Anatase is less dense than rutile and also found to be less stable. The anatase phase however constitutes most of the commercially produced material. Due to its high refractive index and lack of adsorption of visible light, anatase is used as a white pigment for paints, plastics and paper. Current research interests involve photocatalytic properties and its use in optoelectronic devices as well as particle size effects on transformation kinetics and structural stability. Anatase also plays a crucial role in a number of charge-separating devices, like dye-sensitized solar cells or rocking-chair lithium batteries. These devices are based on highly porous films with large surface areas that consist of nano-crystalline anatase.

We [22] have theoretically investigated how the formation of oxygen vacancies and the addition of niobium and chromium atoms as dopants modify the varistor properties of TiO_2 . The calculations were carried out at the HF level using a contracted basis set, developed by Huzinaga et al, to represent the atomic centers on the (110) surface for the large $(\text{TiO})_{15}$ cluster model. The change of the values for the net atomic charges and band gap after oxygen vacancy formation and the presence of dopants in the lattice are analyzed and discussed. The following conclusions were drawn: i) The ab initio calculations show that the formation of oxygen vacancies in TiO_2 leads to a decrease

in the band gap value. ii) Two different valence states of titanium may coexist, probably Ti^{+2} and Ti^{+3} , (iii) The band gap values are strongly affected by the doping process (iv) The global analysis of the results agrees with the experimental data and the physical conception of the performance of the TiO_2 varistor v) Voltage barrier formation and degradation, associated with the band gap, can be explained by a redox reaction between atomic defects. This fact can be of relevance for the understanding of varistor properties of TiO_2 and related materials.

We [28] have made a theoretical quantum mechanical study on TiO_2 , SnO_2 and GeO_2 rutile structures in order to characterize the geometric, mechanical, thermodynamic and electronic properties of these systems. The doping processes of V^{4+} at the sixfold-coordinated site was studied with the aim of determining the relative stability of pure and doped structures. Ab initio perturbed ion calculations with Slater-type orbitals for representing atomic centers and large cluster models was used. Local geometry optimizations have been performed to determine the lattice energy, lattice parameters and bulk modulus, as well as the force constant and vibrational frequencies (ν) of the vibrational modes in the sixfold-coordinated site. Numerical results are analyzed and compared with experimental data, the geometrical distances obtained by computer simulation are in agreement with the reported experimental values. The difference in energy for the substitution of Ti^{4+} , Sn^{4+} and Ge^{4+} for V^{4+} in TiO_2 , to represent these doping processes. The TiO_2 , SnO_2 lattices show a decrease in the ν value from the pure to the doped structure while an opposite trend is obtained for the GeO_2 structure. Recently the (101) surface of the TiO_2 anatase polymorph and its interaction with small Brønsted acid

molecules (H_2O , H_2S and HI) have been studied [65] by means of first-principles molecular dynamics calculations. The structure and the density of states of the relaxed clean surface was computed. Adsorption is predicted to be molecular for both H_2O and H_2S , because of favorable hydrogen bonding interactions with the surface. Only dissociation for HI is preferred, occurring with no sizeable barriers. Ab initio static and dynamic DFT calculations [66] on adsorbed water on TiO_2 (110) confirm that dissociation of H_2O leads to stabilization at low coverages but suggest a more complex picture at monolayer coverage, in which there is a rather delicate balance between molecular and dissociated geometries. Density-functional theory and the pseudopotential method were used to investigate [67] the energetics of adsorption of the molecules H_2O , CH_3OH , H_2O_2 and HCO_2H on the TiO_2 (110) surface. It was shown that the adsorption energy for the most favourable molecular mode of adsorption is extremely close to that for dissociative adsorption in the cases of H_2O , CH_3OH and H_2O_2 . For HCO_2H dissociative adsorption is favoured by a substantial margin, provided the dissociated geometry preserves the equivalence of the two oxygens in the formate ion. The (1x2) adsorption of atomic Cl on the stoichiometric and the reduced rutile TiO_2 (110) surface was investigated [68] from ab initio methods by applying the full-potential augmented plane wave method. According to the calculated adsorption energies of the fully relaxed systems, the most favourable adsorption site is at O defects of the reduced surface. On the stoichiometric surface, Cl is preferentially adsorbed on top of the undercoordinated Ti atoms. Cl 3s and 3p states emptied upon adsorption of Cl on the stoichiometric substrate. The work functions are increased by 1-2 eV, depending on substrate stoichiometry and adsorption geometry.

Recently [69], the interaction of Pd atoms and dimers with the (110) surface of TiO_2 was studied by means of gradient corrected density functional theory (DFT) calculations. $(\text{TiO}_2)_n$ ($n=3-15$) clusters were used to simulate the surface of rutile. The role of embedding in point charges and total ion model potentials was analyzed. A considerable stability of the results versus cluster size was achieved. At low coverage there is a preference for Pd adsorption on the two-fold coordinated protruding oxygens where the bond strength is about 1 eV. Considerable Pd adsorption on the two-fold coordinated protruding oxygens where the bond strength is about 1 eV. Considerable adhesion is found also along the Ti rows, with interaction energies of 0.5 – 0.6 eV. Pd dimers adsorbed on the TiO_2 surface lose most of the Pd-Pd interaction due to the relatively strong bond with the substrate. Adsorption of a CO molecule on the supported Pd dimers shows that the major effect of the bond at the interface is not a modification of the ability of the metal to donate electrons to CO molecules but that of preventing a polarization of the metal electrons away from the CO molecule, thus increasing the Pauli repulsion contribution to the CO-Pd bonding. Recent [70] work presented ab initio periodic Hartree-Fock calculations of the adsorption of small molecules on TiO_2 and MgO . These may be molecular or dissociative, depending on the acidic and basic properties of the molecules in the gas phase and of the nature of the surface oxide. For the molecular adsorption, the molecules are adsorbed as bases on Ti(IV) sites and the adsorption energies correlate with the proton affinities. NH_3 adsorbs preferentially on TiO_2 and CO_2 on MgO . However, this difference or reactivity should not be expressed in terms of acid vs basic behavior, but in terms of hard and soft acidity. MgO surface is a soft acidic surface that reacts preferentially with the soft base,

CO₂. Another important factor is the adsorbate-adsorbate interaction: favorable cases are the sequence of H-bonds for the hydroxyl groups resulting from the water dissociation and the mode of adsorption for the ammonium ions. Lateral interactions also force the adsorbed CO₂ molecules to bend over the surface, so that their mutual orientation resembles the geometry of the CO₂ dimer. A theoretical study [71] of the interaction of CO₂ with the rutile TiO₂ surface using the periodic Hartree-Fock crystal program indicated that the best adsorption mode is obtained when the CO₂ molecules are tilted toward the surface; then, the adsorption mode is also controlled by the adsorbate-adsorbate interactions. Another adsorption mode, competitive with the first one, corresponds to a parallel CO₂ molecule over two titanium atoms. The adsorption over an oxygen atom of the oxide is weak. On the hydrated surface, the presence of hydroxyl groups favors the CO₂ adsorption and leads to the formation of adsorbed bicarbonate ions. Ab initio HF methods were used to study [66] the adsorption of potassium on the (100) surface which indicated that K bonds to the surface via charge transfer of an electron into a particular surface Ti site.

6.5 OTHER OXIDES AND THEIR INTERACTION WITH SPECIFIC ADSORBATES

When TiO₂ is reduced in the bulk, a series of interesting phases [30-35] are formed which consist of slabs of the rutile structure separated by a regular array of shear planes on which the cation density is higher than in TiO₂; these are referred to as Magnéli phases which exist in the composition range between TiO₂ and Ti₂O₃, and their bulk shear plane structure is well understood. When the Ti-O stoichiometry reaches 2:3, a stable, homogeneous bulk phase having the corundum structure results. Each Ti ion in

Ti₂O₃ has one 3d orbital occupied, and pairing of the 3d orbitals of nearest-neighbor Ti ions results in a semiconductor having a 0.1 eV bandgap at room temperature. The Ti-O system can be further reduced to produce the rocksalt oxide TiO_x. This is not as stable as Ti₂O₃, and a wide stoichiometry range exists, with 0.6 < x < 1.28. For compositions close to TiO_{1.0}, the structure distorts to monoclinic, and across the whole stoichiometry range there are substantial densities of both cation and anion vacancies in the bulk. The titanates having the ATiO₃ perovskite structure, in which the A cation has a valence of 2+, are close relatives of TiO₂. This is because the highest filled and the lowest empty A orbitals are significantly farther away from Fermi Levels (E_f) than are the O 2p and Ti 3d levels. Thus the electronic structure in the vicinity of E_f and the vacuum level is dominated by the Ti and O ions. The surfaces of two of these perovskite oxides, SrTiO₃ and BaTiO₃, have been studied on single-crystal samples. LiNbO₃ and LiTaO₃ have the ilmenite structure, but they are electronically related to the perovskite titanates in that they are insulators having filled O 2p valence bands and empty Nb 4d or Ta 5d conduction bands. The V-O system is an even richer and more complex one than Ti-O. Since vanadium can have oxidation states of 2+, 3+, 4+ or 5+, a wide range of stable bulk phases exists. The Magnéli phases for Ti-O also occurs for V-O, so that the number of possible V oxides is very large. The surface properties of vanadium oxides are extremely important since V₂O₅ is an active catalyst for many reactions, including the oxidation and reduction of hydrocarbons, and the oxidation of SO₂ to SO₃, which is used in the manufacture of sulfuric acid. The maximal valency oxide of V is V₂O₅ whose layered orthorhombic structure has only one stable surface face, the basal (001) plane. The rutile oxide VO₂ is one of the most

interesting of the vanadates both because it exhibits a strong semiconductor/metal transition as a function of temperature and since actual vanadia catalysts usually begin as V_2O_5 , but are reduced to lower oxides under reaction conditions. Unfortunately, large VO_2 crystals are difficult to grow. Several experiments have addressed the electronic structure of the V_2O_3 (10 $\bar{1}2$) cleavage face by using a variety of techniques. The main difficulty is that the bulk electronic structure is not very well understood since it is metallic at room temperature, but with quite anomalous electrical and magnetic properties and undergoes around 150 K a transition to a magnetic insulator. Several stable bulk oxides of Mn exist; in fact, Mn exhibits stable oxidation states of 2+, 3+, 4+, 6+ and 7+. The most studied oxide of Mn is MnO, a magnetic insulator having the rocksalt structure. The UHV-cleaved MnO (100) surface is very active for chemisorption with adsorbed molecules which is a distinctly different behaviour from that observed for virtually any other transition-metal oxide. The solid-state chemistry of iron is very different from that of V or Mn. The only two stable oxidation states of Fe in binary oxides are 2+ and 3+, and only three stable bulk oxide phases exist: Fe_xO , Fe_3O_4 and Fe_2O_3 . Fe_xO is a p-type semiconductor which is highly non-stoichiometric and very easily oxidized. Fe_2O_3 is a magnetic insulator with the $3d^5$ configuration. The mixed valence inverse spinel Fe_3O_4 shows high conductivity at room temperature and above. The most stable cobalt oxide is CoO, a magnetic insulator in which Co^{2+} has the $3d^7$ configuration. The most thoroughly studied rocksalt transition-metal oxide is NiO. For the NiO (100) surface the Ni^{2+} ion has a $3d^8$ ground-state configuration. Surface-science experiments on single crystals of Cu oxides have been stimulated in part by the advent of Cu-oxide high-Tc superconductors. The

(111) surface is non-polar, consisting of a plane of Cu ions sandwiched between two planes of O ions. The (100) surface, on the other hand, is polar; ideal, atomically flat surfaces could be terminated by either Cu or O ions. In the ground state CuO has a $3d^9$ electronic configuration and is an antiferromagnetic semiconductor with a bandgap of about 1.4 eV. Problems of surface instability have made it difficult to study the oxides of Mo. MoO_3 , an insulator having a layered orthorhombic structure. The most stable, basal plane is (010), on which only O ions are exposed. At room temperature that surface is quite inert chemically. The MoO_3 (101) surfaces are easily reduced. The 5d-transition oxides WO_3 , Na_xWO_3 and ReO_3 are similar in electronic structure to the early 3d oxides. They have very nearly the ABO_3 perovskite crystal structure, with the W or Re ions occupying the octahedral B cation sites. Stoichiometric WO_3 is an insulator, while ReO_3 is metallic. When Na ions are added to WO_3 we obtain a bulk metallic behavior. Grown single-crystal(110) and (100) RuO_2 surfaces suggest highly non-stoichiometric surfaces. UHV-scraped single-crystal IrO_2 has Ir^{4+} orbitals. The (111) surfaces of ThO_2 and UO_2 is charge neutral and non-polar [30-35].

Regarding chemisorption behavior of specific molecules [1-5, 30-35] we start with the H_2 molecule is non-polar has a very low polarizability and very weak donor or acceptor properties. Thus molecular adsorption is often confined to weak physisorption. The H-H bond is very strong, and dissociation is only possible when the resulting atoms can bond sufficiently strongly to the surface to overcome this. Dissociative chemisorption of H_2 takes place on the most reactive oxide surfaces. We also find a direct interaction of H atoms with a surface. On some surfaces holes (O^-) or other

defects may be required to promote this reaction. H may also bond to metal atoms on some reduced surfaces. There are thus a number of possibilities for dissociative H₂ chemisorption. Homolytic dissociation can result in two OH⁻ or in two metal-hydrogen species. Heterolytic dissociation might also occur. The reactions forming hydroxide are undoubtedly more common and are likely to be promoted by defects such as O⁻. Water has a large dipole moment and lone-pair electrons, and thus is a good donor. Molecular desorption occurs by acid/base interaction with surface metal ions, although this may be quite weak on defect-free low-index surfaces. Stronger adsorption occurs at steps and defects and is often dissociative. CO has only a small dipole moment and in spite of its lone-pair electrons is a very weak donor. Its bonding to transition-metal surfaces is strongly enhanced by the back donation of d electrons into the antibonding π orbital, that is, it acts simultaneously as a donor and acceptor. Since the strength of bonding depends upon availability of d electrons at the surface, adsorption will be favored by low oxidation. CO₂ can act as a weak donor or acceptor. The acceptor character increases when the normally linear molecule becomes bent. N₂O might react with oxygen vacancies to give N₂. NO is more reactive than N₂ or N₂O and adsorbs on many metallic surfaces. NH₃ is a strong donor, and molecular adsorption similar to that for water can occur. Dissociation to adsorbed H⁺ and NH₂⁻ species is also possible in principle. PF₃ reacts with transition metals in a similar way to CO, with the donor properties of the lone pair combined with a π acceptor character. H₂S similar to water, may adsorb either as a molecule or by proton loss (OH formation). SO₂ is capable of a variety of interactions. It can act as a donor or acceptor, but it can also be oxidized or reduced. Molecular adsorption is possible with either S or O atoms bonded to a metal.

Cl₂ is a strong electron acceptor. Xe as one of the noble gases, is chemically inert in most situations and only undergoes physisorption. Oxygen is a powerful electron acceptor and can be reduced in several steps. The complexity of organic molecules makes it more difficult to obtain information from experimental spectroscopies than the inorganic molecules considered above. A general feature of oxide surfaces is the rather facile breaking of C-H but not of C-C bonds although often CO and CO₂ and other species are formed by breaking the carbon framework. For saturated hydrocarbons, such as alkanes, molecular adsorption probably involves only weak dispersion forces. C-H bond breaking may lead to methane coupling reactions. For unsaturated hydrocarbons such as alkenes and aromatics the presence of π -bonding systems lead to the possibility of stronger molecular adsorption. The C-H bond is more acidic and heterolytic dissociation becomes more likely. For alkynes, such as acetylenes molecular adsorption is possible by π interaction. The C-H bond is quite acidic, and heterolytic dissociation is common. Alcohols may undergo molecular adsorption through the oxygen lone pair, or dissociate by deprotonation. For aldehydes molecular chemisorption is possible with the oxygen acting as a donor to a surface acidic (cation) site. For ketones, the oxygen may act as a donor to surface acid sites. The C-H adjacent to the carbonyl group can, however, dissociate heterolytically to give an enolate. For carboxylic acids, molecular chemisorption as well as hydrogen bonding may be possible. Dissociation to carboxylate is also possible. Pyridine, C₅H₅N and dimethyl sulfoxide can undergo molecular chemisorption through lone pairs on N and O respectively. Methyl fluoride is quite unreactive and only physisorbs.

What are some of the adsorbate-oxide interaction not involving (ZnO, MgO, TiO₂)

and SnO₂ [6-29]) the focus of our group's work and of this review paper? In response we note that the following adsorbates are some of the many that participate in important adsorbate-oxide interactions already investigated [1-5,30-35,44,45 and references therein]. Of particular interest are H₂, O₂, H₂O, CO₂, SO₂, CO, NH₃, H₂, OH, O₂, Cl, H₂S, CH₃OH, CH₄, C₅H₅N and CH₃OH adsorption on some of the following oxides: SrTiO₃, CaO, SrO, BaO, α -Al₂O₃, MoO₃, Cr₂O₃, Cu₂O, FeO, Fe₃O₄, Fe₂O₃ with WO₃, Na_xWO₃, MoO_{3-x}, MnO, CoO, V₂O₄, CeO₂, CeGd-oxide, BaCeO₃, LaMo₃, SrCeO₃, SrZrO₃, La₂O₃, Pr₂O₃, V₄P₅O₃₃H₂₁, Li₂O, BaFe₁₂O₁₉, SrO, (VO)₂P₂O₇, VmgO, SCYO, LaCrO₃, LaMnO₃, Nd₂O₃, Sm₂O₃, Y₂O₃ and NiO surfaces of different types. Some recent work [72,73] have focused on the adsorption and reactions at the ((010) and (001) V₂O₅ surfaces; interaction of H₂ with strained rings and vacancy centers at the silica surface [74]; structure and stability of Nb_xO_y and Nb_xO_y clusters by the authors [23]; solid state aspects of oxidation catalysis with emphasis upon the correlation between the presence of mobile ionic defects together with the associated ionic conductivity [31]; adsorption and decomposition of methane on gallium oxide films [75]; adsorption of water at calcium oxide and calcium fluoride surfaces [76]; interaction of H₂ with oxygen vacancy in SiO₂ [77]; H₂O and H₂S chemisorption on Cu₂O (111) [78]. We again emphasize that these are just a few relevant examples of investigations of numerous adsorbate-oxide surfaces reported in the literature.

ACKNOWLEDGEMENTS : We acknowledge financial support from FINEP/PRONEX/FAPESP/CMDC/CNPq (Brasil). W.A.L. was supported by the Director, Office of Science, Office of Basic Energy Sciences, Chemical Sciences Division

of the US Department of Energy under Contract No. DE-AC03-76SF00098.

REFERENCES

1. Taft, C. A., G. Guimarães, T. C. , Pavão, A. C. , and Lester Jr., W. A., 1999, *Int. Rev. Phys. Chem.*, 18, 163.
2. Pavão, A. C., Taft, C. A., Guimarães, T. C., Lester, W. A., Jr., 1994, *Trends Chem. Phys.*, 3, 109 .
3. Pavão, A. C., Taft, C. A., Guimarães, T. C. F., Leão, M. B. C., Mohallem, J. R., and Lester, W. A. J., 2001, *J. Phys. Chem.*,
4. Pavão, A. C., Guimarães, T. C., Taft, C. A., and Lester, W. A., Jr., 1999, *J. Mol. Struct.-THEOCHEM*, 458, 99.
5. Guimarães, T. C., Pavão, T. C., Taft, C. A., and Lester, W. A. J., 1999, *Phys. Rev. B*,
6. Longo, E., Varela, J. A., Senapeschi, A. N., and Whittemore, O. J., 1985, *Langmuir*, 1, 456.
7. Longo, E., Varela, J. A., Santilli, C. V., and Whittemore, O. J., 1985, *Adv. in Ceramics*, 10, 592.
8. Martins, J. B. L., Longo, E., and Andres, J., 1993, *Int. J. Quantum Chem.*, 27, 643.
9. Martins, J. B. L., Longo, E., Tostes, J. G. R., Taft, C. A., and Andres, J., 1994, *J. Mol. Struct.-Theochem.*, 109, 19.
10. Martins, J. B. L., Longo, E., Andres, J., and Taft, C. A., 1995, *J. Mol. Struct.-Theochem.*, 335, 167.
11. Martins, J. B. L., Andres, J., Longo, E., and Taft, C. A., 1995, *J. Mol. Struct.-Theochem.*, 330, 301.
12. Martins, J. B. L., Moliner, V., Andres, J., Longo, E., and Taft, C. A., 1995, *J. Mol. Struct.-Theochem.*, 330, 347.
13. Martins, J. B. L., Longo, E., Andres, J., and Taft, C. A., 1996, *J. Mol. Struct.-Theochem.*, 363, 249.
14. Martins, J. B. L., Andres, J., Longo, E., and Taft, C. A., 1996, *Int. J. Quantum Chem.*, 57, 861.

15. Martins, J. B. L., Taft, C. A., Longo, E., and Andres, J., 1997, *J. Mol. Struct.-Theochem.*, 398, 457.
16. Martins, J. B. L., Longo, E., Taft, C. A., and Andres, J., 1997, *J. Mol. Struct.-J. Mol. Struct.*, 397, 147.
17. Martins, J. B. L., Longo, E., and Taft, C. A., 1998, *Int. J. Quantum Chem.*, 70, 367.
18. Martins, J. B. L., Taft, C. A., Lie, S. K., and Longo, E., 2000, *J. Mol. Struct.-Theochem.*, 528, 161.
19. Almeida, A. L., Martins, J. B. L., Taft, C. A., Longo, E., Andres, J., and Lie, S. K., 1998, *Theochem-J. Mol. Struct.*, 426, 199
20. Almeida, A. L., Martins, J. B. L., Taft, C. A., Longo, E., and Lester, W. A., 1998, *J. Chem. Phys.*, 109, 3671.
21. Almeida, A. L., Martins, J. B. L., Taft, C. A., Longo, E., and Lester, W. A., 1999, *Int. J. Quantum Chem.*, 71, 153
22. Sambrano, J. R., Andres, J., Beltran, A., Sensato, F. R., Leite, E. R., Stamato, F., and Longo, E., 1997, *Int. J. Quant. Chem.*, 65, 625.
23. Sambrano, J. R., Andres, J., Beltran, A., Sensato, F., and Longo, E., 1998, *Chem. Phys. Lett.*, 287, 620.
24. Sensato, F. R., Longo, E., Bulhoes, L. O. S., Santos, J. D., and Martins, J. B. L., 1997, *J. Mol. Struct.-Theochem.*, 394, 259.
25. Sensato, F. R., Filho, O. T., and Longo, E., 2001, *J. Mol. Struct.-Theochem.*
26. Bechepeche, A. P., Treu, O., Longo, E., Paiva-Santos, C. O., and Varela, J. A., 1999, *J. Mater. Sci.*, 34, 2751.
27. Antunes, S. R. M., Santos, J. D., Antunes, A. C., Longo, E., and Varela, J. A., 1995, *J. Mol. Struct.-Theochem.*, 357, 153.
28. Camargo, A. C., Igualada, J. A., Beltran, A., Llusar, R., Longo, E., and Andres, J., 1996, *Chem. Phys.*, 212, 381.
29. Santos, J. D., Longo, E., Leite, E. R., and Varela, J. A., 1998, *J. Mater. Res.*, 13, 1152.
30. Brown, G. E., Henrich, V. E., Casey, W. H., Clark, D. L., Eggleston, C., Felmy, A., Goodman, D. W., Gratzel, M., Maciel, G., McCarthy, M. I., Neelson, K. H., Sverjensky, D. A., Toney, M. F., and Zachara, J. M., 1999, *Chem. Rev.*, 99, 77.
31. Gellings, P. J. and Bouwmeester, H. J. M., 2000, *Catal. Today*, 58, 1.
32. Barteau, M. A., 1996, *Chem. Rev.*, 96, 1413
33. Fujishima, A. and Honda, K., 1972, 238, 37.
34. Henrich, E. and Cox, P. A., *The surfaceScience of Metal Oxides*. 1994, Cambridge: Cambridge University Press.
35. Noguera, C., *Physics and Chemistry at Oxide Surfaces*. 1996, Cambridge: Cambridge University Press
36. Pisani, C., 1999, *J. Mol. Struct.-Theochem*, 463, 125.
37. van Santen, R. A., 1997, *J. Mol. Catal. A: Chem.*, 115, 405 .
38. Minot, C. and Markovits, A., 1998, 424, 119.
39. Lu, X., Xu, X., Wang, N., Zhang, Q., Ehara, M., and Nakatsuji, H., 1998, *Chem. Phys. Lett.*, 291, 445 .
40. Catlow, C. R. A., Ackermann, L., Bell, R. G., Corà, F., Gay, D. H., Nygren, M. A., Pereira, J. C., Sastre, G., Slater, B., and Sinclair, P. E., 1997, *Faraday Discuss.*, 106, 1.
41. Andzelm, J. W., Alvarado-Swaisgood, R. U., Axe, F. U., Doyle, M. W., Fitzgerald, G., Freeman, C. M., Gorman, A. M., Hill, J. R., Kolmel, C. M., Levine, S. M., Saxe, P. W., Stark, K., Subramanian, L., van Daelen, M. A., Wimmer, E., and Newsam, J. M., 1999, *Catal. Today*, 50, 451 .
42. Broadbelt, L. J. and Randall, Q. S., 2000, 200, 23.
43. Neurock, M. and van Santen, R. A., 1999, 50, 445.
44. Whitten, J. L. and Yang, H., 1996, *Surf. Sci. Rep.*, 24, 55 .
45. Gellings, P. J. and Bouwmeester, H. J. M., 2000, *Catal. Today*, 58, 1

46. Rodriguez, J. A., Jirsak, T., and Hrbek, J., 1999, *J. Phys. Chem. B*, 103, 1966.
47. Allouche, A., 1996, *J. Phys. Chem.*, 100, 1820.
48. Pacchioni, G. and Ferrari, A. M., 1999, *Catal. Today*, 50, 533 .
49. Pacchioni, G., 2000, *Surf. Rev. and Lett.*, 7, 277 .
50. Ahlswede, B., Homann, T., and Jug, K., 2000, *Surf. Sci.*, 445, 49 .
51. Shapovalov, V., Truong, T. N., Kovalenko, A., and Hirata, F., 2000, *Chem. Phys. Lett.*, 320, 186 .
52. Chaturvedi, S., Rodriguez, J. A., and Hrbek, J., 1997, *J. Phys. Chem. B*, 101, 10860.
53. Casarin, M., Maccato, C., Tondello, E., and Vittadini, A., 1995, *Surf. Sci.*, 343, 115.
54. Persson, P. and Ojamae, L., 2000, *Chem. Phys. Lett.*, 321, 302.
55. Nakasawa, M. and Samorjai, G. A., 1995, *Appl. Surf. Sci.*, 84, 309.
56. Goniakowski, J. and Gillan, M. J., 1996, *Surf. Sci.*, 350, 145.
57. Lindan, P. J. D., 2000, *Chem. Phys. Lett.*, 328, 325 .
58. Melle-Franco, M. and Pacchioni, G., 2000, *Surf. Sci.*, 461, 54 .
59. Rantala, T. S., Rantala, T. T., and Lantto, V., 2000, *Sens. and Actuators B*, B65, 375 .
60. Rantala, T. S., Rantala, T. T., and Lantto, V., 2000, *Sens. and Actuators B*, B65, 375 .
61. Calatayud, J., Andres, J., and Beltran, A., 1999, *Surf. Sci.*, 430, 213 .
62. Slater, B., Richard, C., Catlow, A., Williams, D. E., and Stoneham, M., 2000, 1235 .
63. Yamaguchi, Y., Nagasawa, Y., Shimomura, S., Tabata, K., and Suzuki, E., 2000, *Chem. Phys. Lett.*, 316, 477 .
64. Dobrovolskii, A., Zyubina, T. S., and Krupnov, B. V., 1995, *Russian J. Inorg. Chem.*, 40, 1553 .
65. Selloni, A., Vittadini, A., and Gratzel, M., 1998, *Surf. Sci.*, 404, 219.
66. Lindan, P. J. D., Muscat, J., Bates, S., Harrison, N. M., and Gillan, M., 1997, *Faraday Discuss.*, 106, 135.
67. Bates, S. P., Kresse, G., and Gillan, M. J., 1998, *Surf. Sci.*, 409, 336.
68. Vogtenhuber, D., Podloucky, R., and Redinger, J., 2000, *Surf. Sci.*, 454, 369 .
69. Bredow, T. and Pacchioni, G., 1999, *Surf. Sci.*, 426, 106.
70. Ahdjoudj, J., Markovits, A., and Minot, C., 1999, *Catal. Today*, 50, 541.
71. Markovits, A., Fahmi, A., and Minot, C., 1996, *Theochem-J. Mol. Struct.*, 371, 219.
72. Witko, M., Hermann, K., and Tokarz, R., 1999, *Catal. Today*, 50, 553.
73. Ranea, V. A., Vicente, J. L., Mola, E. E., and Mananu, R. U., 1999, 442, 498 .
74. Lopez, N., Vitiello, M., Illas, F., and Pacchioni, G., 2000, 271, 56.
75. Kohl, D., Th., O., Geyer, W., Fleishcer, M., and Meixner, H., 1999, *Sens. and Actuators B*, 59, 140 .
76. Leeuw, N. H., Purton, J. A., Parker, S. C., Watson, G. W., and Kresse, G., 2000, *Surf. Sci.*, 452, 9.
77. Lopex, N., Illas, F., and Pacchioni, G., 2000, *J. Phys. Chem.*, 104, 5471 .
78. Casarin, M., Maccato, C., Vigato, N., and Vittadini, A., 1999, *Appl. Surf. Sci.*, 142, 164.