Feature article

Orbital-band interactions and the reactivity of molecules on oxide surfaces: from explanations to predictions

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Abstract. The surface chemistry of oxides is relevant for many technological applications: catalysis, photo-electrolysis, electronic-device fabrication, prevention of corrosion, sensor development, etc. This article reviews recent theoretical works that deal with the surface chemistry of oxides. The account begins with a discussion of results for the adsorption of CO and NO on oxides, systems which have been extensively studied in the literature and constitute an ideal benchmark for testing the quality of different levels of theory. Then, systematic studies concerned with the behavior of adsorbed alkali metals and sulfur-containing molecules are presented. Finally, a correlation between the electronic and chemical properties of mixed-metal oxides is analyzed and basic principles for designing chemically active oxides are introduced. Advances in theoretical methods and computer capabilities have made possible a fundamental understanding of many phenomena associated with the chemistry of molecules on oxide surfaces. Still many problems in this area remain as a challenge, and the approximate nature of most theoretical methods makes necessary a close coupling between theory and experiment. Following this multidisciplinary approach, the importance of band-orbital interactions for the reactivity of oxide surfaces has become clear. Simple models based on band-orbital mixing can explain trends found for the interaction of many adsorbates with oxide surfaces. These simple models provide a conceptual framework for modifying or controlling the chemical activity of pure oxides and for engineering mixed-metal oxides. In this respect, theoretical calculations can be very useful for predicting the best ways for enhancing the reactivity of oxide systems and reducing the waste of time, energy and materials characteristic of an empirical design.

Key words: Oxides – Density functional calculations – Adsorption – Catalysis

1 Introduction

The metal elements are able to form a large diversity of oxide compounds. These oxides adopt a vast number of structural geometries and at an electronic level they can exhibit metallic character or behave as semiconductors or insulators [1, 2]. The surface chemistry of oxides is relevant for many technological applications [1, 3]: catalysis, photo-electrolysis, electronic-device fabrication, prevention of corrosion, sensor development, etc. From a practical viewpoint, one of the most important applications of oxides is in the area of catalysis [1, 3, 4]. In the chemical and petrochemical industries, products worth billions of dollars are generated every year through processes that use oxide and metal/oxide catalysts [3, 4]. In the control of environmental pollution, catalysts or sorbents that contain oxides are employed to remove the CO, NOx and SOx species formed during the combustion of fossil-derived fuels [3–6]. Furthermore, the most active areas of the semiconductor industry involve the use of oxides [7], and in many cases gas-oxide reactions play a predominant role in the fabrication or performance of electronic devices.

Obtaining fundamental knowledge of the factors that control the chemical properties of oxide surfaces is a challenge for modern science and a prerequisite for the rational design of catalysts and other technological devices. Many of these systems are very complex in nature [3, 4, 7]. In principle, when a molecule adsorbs on an oxide surface it can interact with the oxygen and/or metal centers of the substrate. For oxides, it is known that the chemical properties of the metal centers usually depend on the number of oxygen vacancies around them [1, 3]. In addition, there can be big variations in chemical reactivity when changing from one oxide substrate to another [1, 8, 9]. Thus, the main objective is to under-
stand how the structural and electronic properties of a surface affect the energetics for adsorption processes and the paths for dissociation and chemical reactions. Since metal oxides are ionic compounds, the strength of the bond of a molecule with an oxide surface depends on the extent of band-orbital mixing and electrostatic interactions between the charge distribution in the adsorbate and the Madelung field of the oxide [1, 8, 9]. In recent years, advances in instrumentation and experimental procedures have allowed a large series of novel works on the surface chemistry of oxides [1, 8, 10–14]. In many cases, these experimental studies have shown interesting and unique phenomena. Theory is needed to unravel the basic interactions behind these phenomena and to provide a general framework for the interpretation of experimental results [1, 14]. Ideally, using theoretical methods, one should be able to predict patterns in the chemical reactivity of oxide surfaces [15–18].

As in the case of experimental techniques, no single theoretical approach is able to address the large diversity of phenomena occurring on oxide surfaces [1, 15–17]. Oxide surfaces are usually modeled using either a finite cluster embedded in a large array of point charges or a two-dimensional periodic slab [1, 15, 19, 20]. Many articles have been published comparing the results of these two approaches [15, 19–24]. An important advantage of the cluster approach is that one can use the whole spectrum of quantum-chemical methods developed for small molecules with relatively minor modifications. On the other hand, the numerical effort involved in cluster calculations increases rather quickly with the size of the cluster, and for many oxides systems a priori it is not clear how to choose the magnitude of the point charges surrounding the cluster to mimic the effects of the Madelung field [15, 20]. This problem does not exist when using slab models. Owing to the explicit incorporation of the periodicity of the crystal lattice through the Bloch theorem, the actual dimension of a slab calculation depends only on the size of the unit cell [15, 25]. In practical terms, the slab approach is mainly useful for investigating the behavior of adsorbates at medium and high coverages. Very large unit cells are required at the limit of low to zero coverage or when examining the properties and chemical behavior of isolated defect sites in an oxide surface. In these cases, from a computational viewpoint, the cluster approach can be much more cost effective than the slab approach. Slab and cluster calculations can be performed at different levels of sophistication: semiempirical methods, simple ab initio Hartree–Fock (HF), ab initio post-HF (configuration interaction, second-order Møller–Plesset, etc.), and density functional (DF) theory [1, 15–18, 26, 27]. DF-based calculations frequently give adsorption geometries with a high degree of accuracy and predict reliable trends for the energetics of adsorption reactions [17, 18].

This article provides a review of recent theoretical works that deal with the surface chemistry of oxides. A significant fraction of the account is focused on the importance of orbital-band interactions in bonding and how they determine the reactivity of oxide surfaces. The account begins with a discussion of results for the adsorption of CO and NO on oxides, systems which have been extensively studied in the literature and constitute an ideal benchmark for testing the quality of different levels of theory. Then, systematic studies concerned with the behavior of adsorbed alkali metals and sulfur-containing molecules are presented. Finally, a correlation between the electronic and chemical properties of mixed-metal oxides is analyzed and fundamental principles for engineering chemically active oxides are introduced. It is shown that theoretical methods have evolved to the point that they are not only useful for explaining experimental data, but also have predictive power.

2 Adsorption of CO and NO on oxides

In this section, we examine in detail the bonding of CO and NO to MgO(100) and TiO$_2$(110) (Fig. 1). These two substrates are probably the most studied oxide surfaces in the literature [19, 20, 23, 28–30]. Powders of these oxides are used in many industrial applications owing to their low cost [3–5]. The calculated (DF-generalized gradient approximation, GGA) energy positions for the valence and conduction bands of bulk MgO and TiO$_2$ [31] are displayed in Fig. 2. For MgO, the calculations predict a band gap of about 5 eV. Experimental measurements give band gaps of 6–6.5 eV, depending on the techniques employed [1, 22]. The band gap predicted for TiO$_2$ (about 1.5 eV) is also smaller than the