

Tailoring oxide properties: An impact on adsorption characteristics of molecules and metals

Karoliina Honkala

Department of Chemistry, Nanoscience Center, P.O. Box 35, University of Jyväskylä, FIN-40014 Jyväskylä, Finland

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Abstract

Both density functional theory calculations and numerous experimental studies demonstrate a variety of unique features in metal supported oxide films and transition metal doped simple oxides, which are markedly different from their unmodified counterparts. This review highlights, from the computational perspective, recent literature on the properties of the above mentioned surfaces and how they adsorb and activate different species, support metal aggregates, and even catalyse reactions. The adsorption of Au atoms and clusters on metal-supported MgO films are reviewed together with the cluster's theoretically predicted ability to activate and dissociate O₂ at the Au–MgO(100)/Ag(100) interface, as well as the impact of an interface vacancy to the binding of an Au atom. In contrast to a bulk MgO surface, an Au atom binds strongly on a metal-supported ultra-thin MgO film and becomes negatively charged. Similarly, Au clusters bind strongly on a supported MgO(100) film and are negatively charged favouring 2D planar structures. The adsorption of other metal atoms is briefly considered and compared to that of Au. Existing computational literature of adsorption and reactivity of simple molecules including O₂, CO, NO₂, and H₂O on mainly metal-supported MgO(100) films is discussed. Chemical reactions such as CO oxidation and O₂ dissociation are discussed on the bare thin MgO film and on selected Au clusters supported on MgO(100)/metal surfaces. The Au atoms at the perimeter of the cluster are responsible for catalytic activity and calculations predict that they facilitate dissociative adsorption of oxygen even at ambient conditions. The interaction of H₂O with a flat and stepped Ag-supported MgO film is summarized and compared to bulk MgO. The computational results highlight spontaneous dissociation on MgO steps. Furthermore, the impact of water coverage on adsorption and dissociation is addressed. The modifications, such as oxygen vacancies and dopants, at the oxide–metal interface and their effect on the adsorption characteristics of water and Au are summarized. Finally, more limited computational literature on transition metal (TM) doped CaO(100) and MgO(100) surfaces is presented. Again, Au is used as a probe species. Similar to metal-supported MgO films, Au binds more strongly than on undoped CaO(100) and becomes negatively charged. The discussion focuses on rationalization of Au adsorption with the help of Born–Haber cycle, which reveals that the so-called redox energy including the electron transfer from the dopant to the Au atom together with the simultaneous structural relaxation of lattice atoms is responsible for enhanced binding. In addition, adsorption energy dependence on the position and type of the dopant is summarized.

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E-mail address: karoliina.honkala@jyu.fi

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1. Introduction

Metal oxides have long been considered as potential materials for large variety of applications ranging from gas sensing and protective coatings to electrodes in fuel cells, heterogeneous photo (electro) catalysts, and bio-compatible materials [1]. Compared to any other material class both crystallographic and electronic properties of oxides display diverse behaviour, e.g., electronic conductivity ranges from wide-gap insulators to materials with conductivity comparable to metals [2]. The characteristics of oxides can be tailored to improve desired properties in various ways by introducing structural modifications like steps and grain boundaries, adding impurity atoms as dopants, or removing atoms from the structure [1,2]. In particular, point defects such as oxygen vacancies determine optical, electronic, and transport properties of insulating oxides, and they usually dominate the chemistry of its surface [3]. While transition metal oxides are utilized for their catalytic properties, simple oxides such as MgO or CaO are intrinsically inert owing to their very deep valence band and very high conduction band; thus, they are less exploited in applications. However, simple oxides are interesting model systems whose properties have been thoroughly investigated [1,4] and therefore they form an ideal platform to explore the impact of different tailoring strategies to improve their reactivity. One way to achieve this is to prepare oxides as metal grown thin films, which provides an unique approach to modify structural, electronic and chemical properties as a function of film thickness extensively, which is discussed in the reviews of Freund, Pacchioni, and Nilus [5–8]. From the experimental point of view metal supported thin-film systems create specific technical challenges to be tackled. The significant benefit of ultra-thin arrangement of insulating oxides is that they can be studied with scanning tunneling microscopy (STM), which is not possible for their bulk counterparts. Ultra-thin oxide films such as MgO [9,6], NiO [10], CaO [11], Al₂O₃ [12,13], FeO [14–16], and SiO₂ [17] have been extensively studied. A comprehensive overview of metal-supported transition metal oxide films can be found in Ref. [18]. Possible applications of metal supported ultra-thin oxide films can be divided into two groups: support materials and active players in chemical conversions. Gold clusters on metal supported ultra-thin films show distinct features compared to clusters on bulk films [5] and calculations predict that the perimeter of these particles is highly reactive e.g., activating oxygen readily [19]. Supported films can also directly act as a catalyst for CO oxidation [20,21] and dissociate H₂ [22].

Furthermore, metal-supported ultra-thin films are reactive towards water dissociation [23].

Other ultra-thin insulating materials grown on metal surfaces include e.g., NaCl on Cu(111), which is used as a substrate to explore charge transport to nanostructures including Au adatoms [24–26]. While the stoichiometry and atomic structure of ultra-thin MgO corresponds to that of the bulk MgO, this is not always the case. The most prominent example of this is an ultra-thin alumina film over a NiAl support for which determination of atomic structure turned out to be particularly challenging owing to a complex atomic structure. From the interplay between STM experiments and density functional theory (DFT) calculations, the peculiar alumina structure was revealed and it corresponds to Al₁₀O₁₃ being oxygen deficient with respect to bulk Al₂O₃ [12]. Recently, the studies on thin film systems have extended to solid oxide solution thin films on a metal substrate. In the case of NiO–MgO/Mo it was found that the metal support increases the relative stability of the Ni solute at the oxide film [27].

Both experiments and calculations show that metal substrate grown thin oxide layers introduce variable new phenomena. First and foremost charge transfer between electronegative adsorbates such as O₂ and Au, and an oxide–metal interface is generally found to significantly activate an adsorbate and it depends on the film thickness [8]. The occurrence of charge transfer to an Au atom on a Ag-supported MgO film was first predicted by DFT computations [28]. The charge transfer was verified by employing STM measurements to analyse the samples containing Au atoms deposited on a MgO(3ML)/Ag(100) surface at low coverage and temperature [29]. The results highlight the formation of ordered Au adsorption structures owing to charge transfer from the substrate. This picture can be further complicated by the presence of defects and low coordinated sites. The substrate's response to a charged adsorbate comprises the relaxation of lattice atoms near an adsorption site to accommodate the extra charge [30]. Film thickness also affects the metal–oxide interface adhesion, which can be further modified by suitable transition metal dopants [31].

An alternative approach to modify the properties of oxides is to introduce dopant atoms into a host oxide. This can be achieved by replacing a small fraction of the cations in an oxide with different guest cations. Dopants modify the electronic structure and chemical characteristics of an oxide [32] via exchanging electrons with host oxides and adsorbed species. However, dopant atoms can have either lower or higher valence compared to a cation they substitute and

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