Oxide Surface Science

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Abstract
Most metals are oxidized under ambient conditions, and metal oxides show interesting and technologically promising properties. This has motivated much recent research on oxide surfaces. The combination of scanning tunneling microscopy with first-principles density functional theory–based computational techniques provides an atomic-scale view of the properties of metal-oxide materials. Surface polarity is a key concept for predicting the stability of oxide surfaces and is discussed using ZnO as an example. This review also highlights the role of surface defects for surface reactivity, and their interplay with defects in the bulk, for the case of TiO2. Ultrathin metal-oxide films, grown either through reactive evaporation on metal single crystals or through oxidation of metal alloys (such as Al2O3/NiAl), have gained popularity as supports for planar model catalysts. The surface oxides that form upon oxidation on Pt-group metals (e.g., Ru, Rh, Pd, and Pt) are considered as model systems for CO oxidation.
1. INTRODUCTION

Surface science is the study of solid surfaces under well-controlled conditions—usually single crystals and often in ultrahigh vacuum (UHV), i.e., in a background pressure in the range of $10^{-10}$ mbar. Since its inception in the late 1960s, surface scientists have developed techniques that allow insights into the atomic-scale properties of solid surfaces with exquisite precision (1). The invention of scanning tunneling microscopy (STM) and its offspring, atomic force microscopy, has especially broadened the reach of the field. Real-space images with atomic resolution are now routinely achieved with commercial instruments and, in combination with area-averaging spectroscopic techniques, allow one to obtain a truly atomic-scale picture of clean surfaces, and their modification with adsorbed entities. In lockstep with these experimental advances, computational approaches have been developed, in particular first-principles calculations based on density functional theory (DFT). New functionals (2–4) have improved the accuracy of theoretical predictions, and in combination with the expansion of computing power and efficient, user-friendly codes (5), sufficiently large systems can now be modeled so that theory has become invaluable in interpreting experimental data and often guides experiments.

During the past 15 years or so, there has been a shift in the type of systems that surface scientists have investigated: Whereas the initial focus was predominantly on metals and semiconductors, there is a growing body of work that deals with metal-oxide surfaces, the topic of this review.

It is easy to see why one would want to study metal-oxide surfaces. After all, almost every metal is oxidized in the ambient. Hence it is often the surface of the oxide, rather than that of the metal itself, that deserves our interest. In addition, the range of physical and chemical properties of bulk oxide materials is overwhelming. Among metal oxides are superconductors and the best insulators; some oxides are inert enough to act as corrosion protection layers, whereas others are chemically active as catalysts. Some of the most interesting magnetic, optical, and electronic properties are found within this class of materials. Not surprisingly, oxides are at the heart of many established and emerging technologies, and, in many instances, their surfaces or their interfaces with other materials are key to device functioning. Understanding the surface properties of oxides—their geometric and electronic structure, their reaction with adsorbed entities such as molecules or nanoparticles, and the formation of interfaces—is of key interest in many technological areas.

Metal-oxide surfaces are inherently complex systems: Often they can assume a variety of stoichiometries, and even for one particular chemical composition several structural phases can exist. Defects in various forms are prevalent, which adds to their complexity. In fact, the development of sample preparation procedures for appropriate model systems was one of the major roadblocks that had to be overcome before the surface science of metal oxides could develop into the burgeoning field it is today. The systems being investigated can roughly be divided into three classes. The first class contains oxide single crystals, cut or cleaved to expose surfaces of various crystallographic orientations. Most of the bulk oxides that have been thoroughly investigated to date [e.g., TiO$_2$ (6), ZnO (7), and SnO$_2$ (8)] have a band gap of approximately 3 eV and are semiconductors, owing to doping with either intrinsic defects (e.g., oxygen deficiencies in reduced TiO$_2$ samples) or impurities [e.g., hydrogen in ZnO (9)]. Many important oxides are good insulators (e.g., Al$_2$O$_3$, SiO$_2$, or MgO), which hampers the applicability of most experimental surface techniques. Often, these are then synthesized as ultrathin films, i.e., with a thickness of a few atomic layers. Ultrathin oxide films represent the second class of materials that has been investigated quite extensively. Last, but not least, the oxide that forms on top of the metal itself is of high interest. This is especially true for catalytically relevant late transition metals. On their surfaces, it can be the surface oxide, rather than adsorbed oxygen on the bulk metal, that is the catalytically active phase in oxidation reactions.

UHV: ultrahigh vacuum (typically a pressure range of less than $10^{-10}$ mbar)
STM: scanning tunneling microscopy
DFT: density functional theory
Rather than presenting a comprehensive review of all the different systems and phenomena that have been investigated and discovered, we discuss a few fundamental concepts that have emerged as important. We do this by using some of the most investigated and best-understood model systems as examples.

In the first part of this review, we use ZnO as an example of how to consider an oxide structure from a surface point of view. We introduce the concept of surface polarity, which is useful for judging whether a surface is likely stable. It has been recognized early on (10) that defects determine much of the interesting properties of oxide surfaces. In particular they play important roles as adsorption and reaction sites for molecules. These include surface oxygen vacancies, hydroxyls, and line defects such as domain boundaries and step edges, as well as excess cations in the subsurface regions, which may diffuse to the surface at elevated temperatures. STM, as a probe for local electronic structure, is an ideal tool for investigating surface defects. We discuss this aspect in the second part of this review, using the TiO$_2$(110) surface as an example. We then turn our attention to ultrathin metal-oxide films. These form naturally when a reactive metal is exposed to oxygen, but only in rare circumstances do the resulting oxides become well ordered, flat, and epitaxial. For better structural and compositional control, ultrathin metal-oxide films are often synthesized on metallic substrates through evaporation/oxidation, or via oxygen-induced segregation on metal alloys (often used to prepare aluminum oxides on Al-containing alloys). These ultrathin oxide films do not necessarily have the same structure as their bulk counterparts. The same basic building blocks are certainly present, however. Even more importantly from a physical chemistry point of view is that the electronic properties are greatly affected by the underlying metal substrate; hence the reactivity is not the same as their bulk counterparts, and they may exhibit unique properties.

The next section of this review is devoted to the oxidation of late transition metals that are important for catalysis. The structure and stability range of two-dimensional surface oxides, and whether these represent the active phase in the oxidation of CO, are briefly discussed. We then end with a brief outlook of issues that are expected to be even more relevant in the future—for example, more complex (e.g., doped) oxides and the evolving, rich, and interesting field of perovskites.

2. ZINC OXIDE: EXAMPLE FOR A BULK OXIDE AND POLAR SURFACES

Our first example is ZnO, a material of significant importance in catalysis and optoelectronics. It is a wide-band-gap (3.2-eV) semiconductor, and single crystals are readily available. A good overview of the surface chemistry of ZnO has been given by Wöll (7).Interestingly, ZnO can also be grown in the form of nanostructures (11) with fascinating shapes. These small single crystals have well-developed facets, and their promising and exciting properties are often surface-driven or -dominated.

Cox (12) presents a good introduction to the bulk properties of transition metal oxides. Most metal oxides are predominantly ionic in their structural features (12). The bulk lattice consists of (formally) doubly ionized O$^{2-}$ anions, surrounded by metal cations. The ionic radius of O$^{2-}$ is much larger than that of the cations, and the oxygen sublattice typically forms a hexagonally close-packed structure with either an fcc or an hcp-type stacking sequence. The metal cations then reside in the interstices of the close-packed oxygen layers, most often in an octahedral or a tetrahedral configuration, i.e., with either sixfold (6c) or fourfold (4c) coordination, respectively. Alternatively, one can also picture the bulk structure as comprising such octahedral and tetrahedral units that connect in various ways, sharing an edge, a side, or a corner. The example discussed here, ZnO, crystallizes in the wurtzite structure (Figure 1a). The oxygen sublattice forms hexagonally closed-packed layers with hcp-type stacking, and the Zn ions are located in tetrahedral interstices; the tetrahedral units are corner sharing (Figure 1a).
Creating a surface always costs energy, and the minimization of the surface free energy is what drives the energetics of virtually every system. For ionic compounds such as metal oxides, surface polarity is a key concept. Tasker (13) first discussed the surface stability of ionic crystals in a seminal article. A more refined and complete review was provided by Noguera (14) and was recently updated by Goniakowski et al. (15).

Based on purely electrostatic arguments, Tasker classified the surfaces of ionic crystals into three types. He viewed the lattice as comprising charge-neutral layers that lie parallel to the surface and argued that an energetically unstable situation would result if the dipole moment of such a stacking sequence does not vanish.

Type 1 surfaces consist of layers of mixed stoichiometry. These layers carry no dipole moment, and the resulting nonpolar surfaces are often quite stable. For example, the top layer of the ZnO structure in Figure 1a [the (1010) plane] contains an equal amount of Zn and O ions and has no dipole moment. Indeed, the ZnO(1010) surface is the lowest-energy facet of a ZnO crystal (16). We note that the surface Zn and O atoms on ZnO(1010) are both threefold coordinated (3c), providing adsorption sites for molecules. For example, water adsorbs strongly at this surface (17). The oxygen atom of the water molecule is bound to a Zn_{3c} atom, and a dative hydrogen bond to an undercoordinated surface O atom provides additional stabilization.

Tasker type 2 surfaces comprise trilayers containing the same total number of positive and negative charges, but with an excess of one type of charge on each side of the trilayer structure. This results in two opposing dipole moments, which cancel each other. The resulting surfaces are also often quite stable; the classic example is the CaF_2(111) structure, which, for an oxide, is manifested in CeO_2(111). The TiO_2(110) surface discussed in the context of Figure 3 (discussed in Section 3) is such a Tasker type 2 surface.

Type 3 or polar surfaces consist of stacks of bilayers, each one with a dipole moment. For example, the ZnO structure can also be viewed as parallel layers of O anions and Zn cations. In
Figure 1a these layers run in the vertical direction (the structure terminates with an O layer on the left-hand side and a Zn layer on the right-hand side). Indeed, each ZnO crystal that is cut parallel to the basal plane has two surfaces with distinctly different chemical properties (18).

An (0001)-oriented ZnO crystal plate with Zn termination, referred to as a ZnO(0001)-Zn surface, at one side and O termination, ZnO(0001)-O, at the opposite side can be viewed as a series of charged capacitors, as sketched in the equivalent circuit diagram in Figure 1b (14). The electrostatic potential, and thus the self-energy of a crystal with ionic charges, would diverge with thickness. Instead, type 3 polar surfaces undergo a stabilization, which provides a macroscopic depolarization field (14). The form of the stabilization mechanism strongly depends on the system (15). For the case of the ZnO(0001)-Zn surface, many small, triangular islands and holes form (Figure 2a) (19, 20). These islands have a height of half a unit cell (2.6 Å), and each step edge contains only oxygen atoms. This provides excess negative charge on the Zn-terminated...
Ultrathin films: films with a thickness of a few atomic layers; often used as experimental model systems for highly insulating oxides.

Surface and stabilizes the surface for a wide range of oxygen chemical potentials (20). On the ZnO(0001)-O surface, a different stabilization mechanism is operational. The surface is flatter; the islands are hexagonal; and most step edges are one unit cell high (5.2 Å) and contain both Zn and O atoms (Figure 2b). There are strong indications that a (1×1) terminated ZnO(0001)-O surface is fully covered with hydrogen (7, 21). It was also suggested that a clean, hydroxyl-free ZnO(0001)-O surface exhibits a (1×3) reconstruction, although this issue has remained controversial (22). As pointed out by Goniakowski et al. (15, 23), the rules for surfaces polarity compensation are lifted in the case of ultrathin films and nanostructures. Indeed, ultrathin ZnO films grown on Ag(111) have a depolarized, flat (graphitic) structure (24).

Clearly, the stabilization mechanism dramatically affects the surface chemistry of the polar ZnO surfaces. For example, the cation-anion pairs at the many step edges on the ZnO(0001)-Zn side provide active sites for the dissociation of Brønsted acids (25, 26), and a fully hydroxylated (1×1) ZnO(0001)-OH surface is quite different from an H-free (reconstructed) one.

3. TITANIUM DIOXIDE: EXAMPLE FOR SURFACE AND BULK DEFECTS

Our next example is TiO₂, more specifically the (110) surface of rutile, the thermodynamically most stable structural TiO₂ polymorph. Diebold (6) reviewed the surface science of TiO₂ in 2003, and Pang et al. (27) present a more recent account, focusing exclusively on the surface chemistry of TiO₂(110). The TiO₂(110) surface has received significant attention in the surface-science literature. Again, it is the versatility of this material, and the multitude of its applications [e.g., in photocatalysis (28)], that makes its surfaces so interesting. Surface-science studies have also been motivated by the fascinating observation that nanosized Au clusters are capable of catalyzing oxidation reactions at low temperatures (29). TiO₂ is the prototypical support for such nanostructured Au clusters, and it is a challenging and rewarding puzzle for surface scientists to disentangle how each component of the system—the cluster (e.g., its size, shape, and electronic structure), the support, and the interface between the two—contributes to the catalytic process. TiO₂ is relatively easy to handle experimentally, which has contributed considerably to its popularity as a model system. Many vendors provide rutile single crystals, and standard UHV sample preparation procedures (i.e., sputter-cleaning with rare-gas ions and annealing) can be used to prepare flat surfaces with wide terraces. This treatment results in an oxygen-deficient (or Ti-rich) bulk, easily recognized by a color change from transparent-yellowish to blue (30). On the one hand, this provides a considerable practical advantage, as reduced samples have high electrical conductivity and are amenable to all surface analytical techniques involving charged particles. On the other hand, the fact that the bulk contains defects that might migrate to the surface needs to be considered when studying the surface properties of TiO₂ (30–33).

A model of the TiO₂(110) surface is shown in Figure 3a. It terminates in a (1×1) structure with some relaxations as predicted by DFT calculations and as confirmed by recent diffraction studies (34, 35). The surface consists of rows of Ti₅c atoms, running along the [001] direction, separated by twofold coordinated (or bridge-bonded) surface O₂c atoms. (Although O₃c atoms also reside on the selvedge, they are not considered surface atoms as they have the same coordination as in the bulk.) The Ti₅c atoms act as (Lewis) acid sites for the adsorption of lone-pair molecules and the O₂c atoms as Brønsted bases, which can accept an H atom from an adsorbate.

The STM image of the TiO₂(110) surface shown in Figure 3b was taken in the constant-current mode by tunneling into empty states. This imaging mode is typical for n-type semiconducting oxides. The bright and dark lines along the [001] direction are located at the position of the Ti₅c and O₂c sites, respectively. The image contrast is dominated by electronic effects: The
Figure 3

The TiO$_2$(110) surface with O vacancies (O$_{vac}$) and OH groups. (a) Geometric model. The OH group with the green O atom stems from the water molecule that has filled a vacancy, and the red one represents a lattice O$_{2c}$ atom that has received a proton upon water dissociation. (b) Scanning tunneling micrograph (100 Å × 100 Å, $V_{\text{sample}} = +1.48$ V, $I_{\text{tunnel}} = 0.08$ nA). (c) Photoemission spectrum taken with a photon energy of 47 eV. The right and left insets show the gap state and the region of the OH 3σ states, respectively, and the dashed blue line marks the position of the valence band maximum.

conduction band consists mostly of Ti states, and the Ti$_{5c}$ atoms appear higher in the STM, even though they do not stick out of the surface as far as the O$_{2c}$ atoms (Figure 3a) (36). STM is, after all, a technique that foremost probes the local electronic structure.

On vacuum-prepared TiO$_2$(110) surfaces, a few percent of the bridging O$_{2c}$ atoms are typically missing. The resulting vacancies appear as the (fainter) bright spots on the dark rows in STM. That O vacancies can be observed so readily, and that defect-mediated reactions can be monitored directly with atomic-scale resolution (37–40), is one of the attractive features of TiO$_2$ as a model system for surface reactions. For example, water dissociates at the vacancies, resulting in two hydroxyls (37–42) as shown schematically in Figure 3a. [It seems that these two hydroxyls should be equivalent, although STM results indicate a different diffusivity (40).] The OH groups usually appear a little brighter than the O vacancies in STM images (38). It has long been known that water adsorbs on TiO$_2$(110) with a sticking probability of unity up to very high temperatures (43) and that good vacuum conditions are needed to observe nonhydroxylated O vacancies. This fact,
which was pointed out early on (42, 44), has been overlooked in some cases (45), leading to much initial confusion about defect motion and chemistry on TiO$_2$ (45, 46).

Defects modify the electronic structure of TiO$_2$. This can clearly be observed with spectroscopic techniques, for example, in the photoemission spectrum in Figure 3c. The binding energy scale in Figure 3c is referenced to the Fermi level (E$_F$), which is located close to the lower edge of the conduction band in this $n$-type semiconductor. The valence band maximum is located at approximately 3 eV, consistent with the band gap of TiO$_2$. [The exact position of the valence band maximum depends on the photoemission geometry in this indirect semiconductor (47).] The feature at approximately 1-eV binding energy, a Ti-$3d$-derived (48) band gap state, is only present on nonstoichiometric TiO$_2$ surfaces. When such a slightly defective surface is exposed to water at room temperature, the gap state increases a little in intensity and shifts to somewhat higher binding energies. Features that are indicative of surface hydroxyls appear as well, i.e., the $3\sigma$ state at approximately 11-eV binding energy and a $1\pi$ state within the valence band.

It seems quite straightforward to interpret the gap state as coming from O vacancies and hydroxyls on the clean and water-dosed surface, respectively. There have been some recent controversies about this assignment, however (49, 50). Based on DFT with the revised Perdew-Burke-Ernzerhof functional (51), it has been claimed that O vacancies do not cause a gap state, and that Ti interstitials, residing in the near-surface region, are responsible for the gap state and for surface chemical reactions observed with STM (49). In these authors’ opinion, it is probably both O vacancies and Ti interstitials that contribute to this state. DFT calculations using standard functionals do not show a clearly separated band gap feature and tend to delocalize the extra electrons across the slab rather than localizing it at the position of the O vacancy. The difficulties of treating correlation effects in metal oxides with standard DFT have been pointed out by Ganduglia-Pirovano et al. (52). Calculations using Hartree-Fock or hybrid DFT methods result in a gap state for both an O vacancy and a hydroxylated O$_{2c}$ atom (53).

As briefly mentioned above, that Ti interstitials reside in the TiO$_2$ lattice has long been recognized as an important feature of TiO$_2$ surface chemistry. In a series of elegant experiments, using isotopically labeled Ti and O, Henderson (54) demonstrated that Ti interstitials diffuse much more readily than O vacancies. This has to be considered, for example, when reduced TiO$_2$ is annealed in an oxygen atmosphere (31–33), in which reoxidation processes can result in metastable surface structures or in other oxidation reactions that occur at somewhat elevated temperature (55). It is good to see the renewed interest in this issue.

Several interesting aspects of TiO$_2$ surfaces deserve further investigation. For example, the structure of another rutile surface orientation, the TiO$_2$(011)-(2\times 1) surface, has recently been resolved (56, 57). This surface is quite stable with a fairly low surface energy. With a large unit cell and high corrugation, it is well-suited for STM studies (58). Different from the TiO$_2$(110) surface, TiO$_2$(011)-2\times 1 is hydrophobic in the absence of defects (59); hydroxyls nucleate the growth of one-dimensional, H-bonded water clusters. That linear arrays of O vacancies can be produced by electron bombardment (60) should be an attractive feature for controlling defect-mediated surface chemistry at the atomic level.

The anatase polymorph of TiO$_2$ is also a promising subject for further surface investigations (61). Anatase is used in most technical applications, and most nano-TiO$_2$ is of the anatase form. Interestingly, the surface oxygen vacancies that are so prevalent on rutile tend to migrate to subsurface sites on TiO$_2$ anatase (101) (62, 63). This could be particularly relevant for defect-mediated surface chemistry, as subsurface vacancies may survive in ambient conditions, outside of a vacuum chamber. Also, important adsorbates such as water form unique and interesting structures (64) on TiO$_2$ anatase (101).
4. ULTRATHIN OXIDE FILMS

4.1. Reactive Evaporation

Ultrathin metal oxides have been produced by vapor deposition of a metal on an appropriate (mostly metallic, and often refractory) single-crystalline substrate and by oxidation of the resulting overlayer either during or after deposition. Ideally, this produces an epitaxial film that has a known, reproducible structure and that is thin enough to avoid charging problems in STM and surface spectroscopies. Metal nanoclusters are often deposited on top of these ultrathin metal-oxide films, and the resulting samples are used as planar model catalysts (65). The supported nanoclusters are again grown by simply vapor depositing a metal—the low surface energy of most metal oxides and the low interface energy (weak binding) between the oxide and late transition metals lead to the formation of three-dimensional clusters. Systems include MgO (66, 67) and SiO$_2$ (68), as well as many transition metal oxides such as iron oxides (69), titanium oxides (70), vanadium oxides (71–73) (Figure 4), and cobalt oxides (74). For a more extensive discussion, the reader is referred to several excellent review articles on this topic (e.g., see 65, 71, 75, 76).

Many different oxide phases and structures are formed upon reactive evaporation; such phases can often coexist. This is especially true for transition metals, which are stable in various oxidation states. Some phases are similar to bulk structures, whereas others exist only as ultrathin films and may exhibit special electronic or magnetic properties. In addition to the exact preparation parameters (e.g., temperature, O$_2$ pressure, and growth rate), the substrate is also important; the same metal-oxide film, prepared with similar experimental parameters, often exhibits a different structure depending on the type of metal used. A nice example is vanadium oxides, which have been investigated extensively by the Netzer group (71, 72) (see Figure 4).

Figure 4

(a) Scanning tunneling microscopy (STM) image of a vanadium oxide film, grown by reactive evaporation on Rh(111). (b) STM image showing star-like V$_6$O$_{12}$ clusters that form upon further oxidation of the film. The inset shows the geometry obtained by density functional theory. Figure adapted with permission from Reference 73. Copyright (2004) by the American Physical Society.
Recently, it has been pointed out that a key difference between ultrathin films and bulk oxides is the facile charge transport through the films via tunneling. For example, in ultrathin MgO films, adatom energy levels are shifted with respect to the same adatom on the bulk oxide (67, 77, 78). This charge transfer does not occur instantaneously; it has been argued that the timescale is on the order of $10^{-15}$ s or longer (79).

4.2. Alumina on NiAl

In addition to reactive deposition, the oxidation of metal alloys has been used as a convenient way to form ultrathin metal-oxide films. With a formation enthalpy of 1676 kJ mol$^{-1}$ (5.79 eV per oxygen atom), $\alpha$-Al$_2$O$_3$ (corundum) is one of the most stable oxides. It is responsible for the corrosion resistance of the otherwise highly reactive Al metal. Oxidation of pure Al does not produce any well-ordered oxide films (80), but a smooth alumina film was found after oxidation of a NiAl(110) alloy surface at elevated temperatures (81, 82). The resulting ultrathin film has been used in numerous surface and model catalysis studies (75, 76, 79). Its structure was solved by a combination of STM and DFT (83) (Figure 5). It is only $\approx$5 Å thick and consists of four layers: an interfacial Al layer (Al$_i$), an oxygen layer (O$_i$), a layer of Al atoms (Al$_s$) directly above the O$_i$ atoms, and finally the surface oxygen layer, O$_s$. Although all bulk structures of alumina consist of (distorted) hexagonally close-packed O layers, the O$_s$ atoms in the ultrathin alumina film are arranged in squares and triangles. The short-range order in the film is similar to the bulk oxide, however: Together with the O$_i$ atoms below, the O$_s$ triangles form tetrahedra around the Al$_s$ atoms. The O$_s$ squares can be viewed as truncated octahedra, each with an Al$_s$ atom close to the center (Figure 5b). Oxygen octahedra and tetrahedra are building blocks of various polymorphs of aluminum oxide, whereas, in corundum, all Al atoms are octahedrally coordinated. This is one

Figure 5

The surface aluminum oxide on NiAl(110). (a) Scanning tunneling microscopy (STM) image with calculated positions (density functional theory) of the surface oxygen atoms superimposed (red circle). (b) Top view of the structure model. Marked in yellow are a square (truncated octahedron) and a triangle (truncated tetrahedron) of O$_i$ atoms. (c) Side view with interlayer distances. (d) Wide-scale STM images with line defects (light gray), which act as nucleation sites for Pd clusters. (e) Equally spaced Pd clusters on an ultrathin alumina film on Ni$_3$Al(111). Panel e taken from Reference 96, reproduced by permission of The Royal Society of Chemistry.
of the recurring motifs in ultrathin oxides: The structure is different from any bulk phase but comprises the same building blocks.

The ultrathin alumina film has a stoichiometry of $\text{Al}_{10}\text{O}_{13}$; in the literature these films are nevertheless often referred to as $\text{Al}_2\text{O}_3$. Although the film seems oxygen deficient at first glance, it has a large band gap of $\approx 6.7$ eV (84), not too different from the one of bulk $\text{Al}_2\text{O}_3$ (9 eV), indicating a stoichiometric oxide. Based on DFT calculations, one can argue that the $\text{Al}$ atoms are not fully oxidized. Their $p_z$ orbitals bind to the substrate, and thus their formal valency should be considered $\text{Al}^{2+}$; this renders the whole oxide charge neutral (83). With a stacking of $\text{Al}^{2+}$–$\text{O}^{2-}$–$\text{Al}^{3+}$–$\text{O}^{2-}$, the alumina film has a net dipole moment; in contrast to thick materials, this does not pose a problem for such an ultrathin film (15). Frequently found line defects (domain boundaries) in this oxide are oxygen deficient. This deviation from charge neutrality results in band gap states as well as band bending (85). These line defects act as preferred nucleation sites for the growth of supported nanoclusters (see Figure 5).

Heterogeneous nucleation: nucleation at surface defects during film or cluster growth; the most common growth mode for metals on metal-oxide surfaces

In contrast to many of the ultrathin oxides on Pt-group metals discussed in the next section, an ultrathin alumina film is not thermodynamically stable (86). It owes its existence to kinetic limitations: The film cannot grow in thickness because molecular oxygen from the gas phase does not dissociate on the oxygen-terminated surface. Further oxidation can be accomplished by oxygen dissociation on metal clusters grown on the oxide film. The atomic oxygen spills over (87) onto the oxide, and a thicker oxide film forms (88). In addition to $\text{NiAl}(110)$, similar ultrathin aluminium oxides have been found to form on $\text{Ni}_3\text{Al}(111)$ (89–91), $\text{Cu}_{91}\text{Al}_{9}(111)$ (92), and probably $\text{NiAl}(100)$ (93). In all these alloys, Al is combined with a less reactive metal that has a higher melting point. The slow supply of Al, as it diffuses to the alloy surfaces, is an important ingredient for forming these well-ordered ultrathin oxides.

The growth of, and chemical reactions on, alumina-supported clusters was studied extensively as models for catalysts (75, 76, 79, 94). For room-temperature deposition, the clusters of most late transition metals form at defect sites of the ultrathin alumina films. Clearly, surface diffusion of adatoms is fast enough to find a defect (heterogeneous nucleation) before enough adatoms meet to form a stable cluster on the perfect surface (see Figure 5d for an example of nucleation of Pd at line defects). A notable exception is Pt, which forms a large number of nuclei (79), as do more reactive metals that bind strongly to oxygen, e.g., vanadium (95). An alumina film on $\text{Ni}_3\text{Al}(111)$ represents a particularly nice example of how heterogeneous nucleation can be used to produce a well-defined planar model catalyst (90, 91, 96). This film contains a hexagonal arrangement of holes with a separation of 41 Å. These holes act as nucleation sites for metal clusters; with vapor deposition, equidistant clusters form with a narrow size distribution. Whereas ultrathin alumina films represent convenient and useful model systems for heterogeneous catalysis, one has to be aware of the limited thermal stability of some supported clusters. Nickel diffusion through the oxide film into the metal substrate was observed at temperatures as low as 480 K (97); Co clusters are stable only up to $\sim 600$ K (98).

5. SURFACE OXIDES OF PLATINUM-GROUP METALS AND CATALYSIS

One of the long-time goals of surface science, honored by the award of the 2007 Nobel Prize in Chemistry to Gerhard Ertl, is a better understanding of catalysis. The oxidation of CO on Pt-group (Group VIIIb) metals is possibly the most-investigated catalytic reaction in surface science. CO oxidation serves as a model for more complex reactions, and it also has technological relevance for the purification of automotive gas exhaust. The reaction $\text{CO}_{\text{ads}} + \text{O}_{\text{ads}} \rightarrow \text{CO}_2$ is deceivingly simple. Nevertheless, recent work has pointed out that, rather than combining an adsorbed CO with an O adatom on the metal surface, oxidic species may play a decisive role.
Figure 6
Structure of the surface oxides on (a) Pd(111) and (b) Rh(111). A Pd₅O₄ unit is marked in panel a and the upper layer in the bottom-right corner of panel b is removed to show the stacking. (c) Density functional theory–calculated surface phase diagram of the Rh(111) surface as a function of the chemical potential of oxygen, $\mu_O$, (based on 122). For conversion from $\mu_O$ to experimental parameters, one can use the upper x axis and a scale bar corresponding to a change of pressure by a factor of 10 at 700 K. The most stable structures with increasing $\mu_O$ are two oxygen adatom phases, first with a (2×2) structure and then a (2×1) structure, followed by Rh₂O₃. The trilayer surface oxide depicted in panel b is only metastable but stabilized by kinetic effects.

For more reactive metal catalysts, such as Ru, a (bulk-like) RuO₂ oxide layer forms under high-pressure conditions, and the CO is oxidized by the oxygen from the RuO₂ surface in a Mars-van-Krevelen mechanism (99). (That RuO₂ does not form under UHV conditions led to the puzzling observation that Ru, which is a very active catalyst under atmospheric conditions, is nonreactive at low pressures.) For the more noble metals Pd, Pt, and Rh, an ultrathin surface oxide forms under conditions at which the catalyst is most active (100–105). Such a surface oxide does not necessarily resemble a bulk phase but may have its own, unique structural features. The exact structure of surface oxides, the range of their stability, and whether the surface oxide or a layer of adsorbed oxygen layer is catalytically most active are contentious issues to this day (106, 107).

Lundgren et al. (108) have reviewed the surface oxides on close-packed late transition metals. Shown in Figure 6a,b are two prototypical structures. For Pd, strictly two-dimensional, almost flat layers form (109–112). Figure 6a illustrates the surface oxide of Pd(111) (109). It has a Pd₅O₄ stoichiometry, and, similar to the alumina case discussed above, it is different from the bulk oxide, PdO. The Pd atoms in this structure are accessible to gas-phase species; hence CO can adsorb (113). On low-index Rh surfaces, conversely, so-called trilayer surface oxides form (114–116) (see Figure 6b). These consist of three close-packed layers: a lower (interfacial) O layer, an Rh layer within the oxide, and an O layer at the top. The termination with such a close-packed O layer makes Rh surface oxides inert (at least at the low pressures compatible with UHV experiments); it has been shown that the reduction of the surface oxide starts at defects and proceeds at the boundary between reduced areas and the surface oxide (117, 118).

The stability range of surface oxide phases can be assessed using first-principles thermodynamics (119, 120). Figure 6c shows the surface phase diagram for Rh(111) as an example. Plotted is the (generalized) surface energy obtained from DFT calculations as a function of oxygen chemical potential $\mu_O$, which is a function of the oxygen pressure $p_{O_2}$ and temperature $T$. For each
structure, the surface energy depends linearly on $\mu_O$ and is derived in the following way: The slope of the line is given by the oxygen coverage, and $\mu_O$ at the intercept with the (horizontal) line for the clean metal surface equals the O adsorption energy. For each $\mu_O$ value, one particular structure has the lowest surface energy; this is the one that will form in thermodynamic equilibrium. [Entropy effects typically play a minor role (121) and are not considered in Figure 6c and similar surface phase diagrams.] The phase diagram in Figure 6c predicts that the most stable structure consists of O adatoms with a coverage ($\theta$) of 0.5 monolayers for chemical potentials between $−1.54$ eV and $−1.25$ eV. For more O-rich conditions, with chemical potentials higher than $−1.25$ eV (to the right of the vertical line in Figure 6c), the bulk Rh$_2$O$_3$ structure is the most stable one. We note that the trilayer surface structure, which is observed experimentally (Figure 6b), is not a thermodynamically favored structure at any value of $\mu_O$, but a kinetically limited phase (114, 122). Such surface phase diagrams can also be extended for cases in which several gases are present [e.g., O$_2$ and CO (120)] and can predict phases under reaction conditions that are often not accessible in surface experiments.

The discovery of surface oxides, together with the development of surface-science techniques that can operate under reactions at realistic (high) pressures, has motivated further studies of CO oxidation on Pt-group metals. It was discovered that high activity for CO oxidation on Pt, Pd, and Rh coincides with the presence of ultrathin oxides (100–105); similar conclusions were also drawn from X-ray absorption spectroscopy measurements of real catalysts (123). In contrast, molecular-beam experiments in UHV show a higher catalytic activity for the oxygen adatom phase than for the surface oxide on Pd(111) (124). For other Pt-group metals, there are also indications that the highest activity occurs at an oxygen coverage below that of surface oxides (106, 107, 125). These results are not necessarily contradictory, however. At high $\mu_O$, oxygen adatom phases are often not stable (e.g., see Figure 6c); thus even if these would be the more reactive phase, they may not form at high (atmospheric) pressures and moderate temperatures. CO-saturated metal surfaces are inactive because they block O$_2$ adsorption, so it is possible that a surface oxide remains as the only phase with appreciable reactivity. Furthermore, DFT calculations suggest a high reactivity at the boundary of surface oxides (126), which may be especially important for oxygen-terminated surface oxides, such as the ones found on Rh surfaces. The dispute about these questions is far from settled, however.

6. OUTLOOK

Much of the research reviewed here has been motivated by the desire to better understand—and, ultimately, design—heterogeneous catalysts. The increase in the consumption of the world’s natural resources and the related environmental problems will only intensify the search for more efficient and selective catalysts (127). Oxides have long been recognized as an important component of catalysts, as a support that often critically affects functioning (128, 129), as well as the active component itself. Many important issues have been addressed, but even more remain open—for example, whereas (intrinsic) surface defects have received extensive attention, dopants and impurities (which, after all, are most often used to functionalize technical materials) are comparatively unexplored at the atomic/molecular scale (130). The synthesis of ultrathin metal-oxide films has opened the fascinating opportunity of producing nanostructures with intriguing geometries and potentially interesting properties, but these samples might have limitations in mimicking an insulating support. Thus there is a push to refine experimental methods that allow the monitoring of fully insulating systems. Ideally measurements are performed in operando, i.e., under realistic pressure/temperature conditions, and with a time resolution that allows the observation of the dynamic changes of the catalyst. Clearly, more complex systems need to be explored, without losing...
the control provided by UHV-based studies of reductionist, simple systems. Moving from metals to oxides has represented an important step in surface-science research; moving from simple to more complex oxides needs to follow in both theory and experiment.

The surface-science community has rallied around a few, select metal oxides, and has made great strides in understanding their atomic-scale properties. There is still a knowledge gap, however, for many materials that are interesting and important in their own right, but have not been explored in depth. To judge which surface phenomena are materials specific and which ones can be generalized, it is necessary to broaden the numbers and kinds of systems that are studied with the same thoroughness as, say, TiO_2. SnO_2, for example, also has the rutile structure but is not a transition metal oxide. A key consideration for the stability of tin oxide surfaces and step-edge structures (8, 131) is that the cation is only stable in two oxidation states, an aspect that is not relevant for TiO_2.

An important class of materials, for physical chemists, materials scientists, and condensed matter physicists alike, is the perovskite-type oxides. They find diverse applications, for example, in solid oxide fuel cells, or in devices based on their piezoelectric, ferroelectric, superconducting, or magnetoresistive properties. The richness of their physical properties has provided a platform for much exciting research in condensed matter physics and offers unique opportunities for surface science (132, 133). Many of the fascinating phenomena of these materials are interface driven (134), and there is still much to be learned about the surface properties of these systems (135). For example, the key role of surface preparation, central to more chemistry-oriented research, is often not enough appreciated (136). Yet it should be even more important in complex, multicomponent materials, in which properties sensitively depend on the details of the system.

**SUMMARY POINTS**

1. Most metals are oxidized in the ambient, and metal-oxide materials have a large range of physico-chemical properties, which makes them useful for many applications. In virtually all of these, surfaces play a role. This motivates surface-science studies of well-characterized metal oxides, with a reproducible, known structure.

2. Defects on metal oxides affect the local structural and electronic properties and are often chemical reaction centers. With local probes (such as STM), chemical reactions at the atomic scale can be visualized.

3. Polar oxide surfaces have a nonvanishing dipole moment and are intrinsically unstable. Although they can be stable as ultrathin films and nanostructures, various stabilization mechanisms are at work for thicker materials.

4. Ultrathin oxide films, formed by oxidation of a metal overlayer on an appropriate substrate, or through oxygen-induced segregation of one component (e.g., Al) of an alloy, can have structural and electronic properties that are quite different from their bulk counterparts. When decorated with metal nanoclusters, such ultrathin oxide films are useful as planar model catalysts.

5. First-principles thermodynamics based on DFT calculations that account for the chemical potential of the gas phase are useful for predicting the stability range of metal-oxide phases.

6. In catalytic oxidation processes, the surface oxides of late transition metals (platinum group) play an important role, although many open questions remain.
7. Future directions include the study of more complex oxides, in environments relevant for catalysis research, and the broadening of the material systems investigated, for example, to perovskites.

DISCLOSURE STATEMENT

The authors are not aware of any affiliations, memberships, funding, or financial holdings that might be perceived as affecting the objectivity of this review.

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LITERATURE CITED


5. Describes the VASP code, one of the most popular DFT-based program packages; it has been used extensively to model the surfaces of oxides and other systems.


13. Gives a tutorial introduction into the stability issues related to polar surfaces, based purely on electrostatics; a more modern approach is followed in Ref. 14.

36. Was one of the early STM works on point defects on TiO2(110) and established how to interpret the STM image contrast; Ref. 38 unequivocally showed how to distinguish oxygen vacancies from hydroxyls.


54. Showed that defect diffusion through the TiO₂ bulk is more facile for Ti interstitials than O vacancies.


99. Established that the catalytic reactivity of Ru results from an oxidized surface layer.

100. Discovered that high catalytic activity coincides with the presence of a surface oxide on Pt.
121. Discusses first-principles thermodynamics based on DFT calculations.