## 10. Thin Oxide Films as Model Systems for Heterogeneous Catalysts

Hans-Joachim Freund D, Markus Heyde D, Helmut Kuhlenbeck D, Niklas Nilius D, Thomas Risse D, Swetlana Schauermann, Thomas Schmidt D, Shamil Shaikhutdinov, Martin Sterrer D

This chapter summarizes efforts to use thin oxide films as model supports for heterogeneous catalysts. We demonstrate that the oxide film route provides a useful platform to study oxide surfaces, per se its interaction with species from the gas phase, supported metal and oxide nanoparticles using the entire tool box of surfaces science under ultrahigh vacuum conditions. The extension to use thin oxide films as template also under ambient conditions or under water, is discussed and the potential to use oxide films as genuine two-dimensional materials is exemplified with vitreous and crystalline silica films.

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#### 10.1 Preamble

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"A detailed understanding of processes at surfaces requires knowledge of the surface structure at the atomic scale. Unraveling this knowledge for metal surfaces caused the success of surface science and its application to chemical reactions at surfaces and heterogeneous catalysis culminating in the 2007 Nobel Prize for *Gerhard Ertl* [10.2]. The surface science approach was limited for quite a while to metal single crystal surfaces. Only in the midnineties, the books by *Cox* [10.3], by *Henrich* and *Cox* [10.4] as well as by *Noguera* [10.5] on oxide surfaces alerted the broader community that

this important class of materials should also be included into consideration of surface scientists. The field of oxide surface science has been developed since. The oxide single crystal surface for which most of the data have been published is  $TiO_2(110)$  [10.6,7]. *Henrich* and *Cox* [10.3,4] also pointed out that reproducible preparation is at the heart of studies on oxide surfaces, specifically bulk single crystal surfaces. Based on this comment researchers started to think about alternative routes to reproducibly prepare oxide surfaces, which led to the birth of thin oxide film surface science [10.8–17]. The idea was to grow oxide films on metal single crystals using the rules of epitaxial growth. If made sufficiently thin, surface charg-

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**Fig. 10.1a-f** Schematic illustration of various thin film systems and scenarios. Reprinted (adapted) with permission from [10.1] Copyright (2016) American Chemical Society

ing, which hampers the investigation of insulating bulk oxides when using charged information carriers, such as electrons or ions, does not occur. The field has further developed tremendously in recent years. Two books [10.18, 19] and a number of review articles have been published on the subject [10.8–17] providing the reader with an impression of what has been achieved. A wide variety of techniques has been applied to study oxide thin films, as collected therein. The present chapter will discuss a number of examples, mainly from the laboratories of the authors, to demonstrate how the field has developed and to highlight interesting avenues for future research in this area.

Before we discuss specific examples, we would like to address a few general scenarios, as schematically indicated in Fig. 10.1. Figure 10.1a shows an oxide film of a thickness chosen in such a way that the buried interface between oxide film and metal support does not influence the surface properties of the oxide film. Molecules, metal or compound (for example another oxide) nanoparticles, deposited and adsorbed on the surface, would experience the same geometric and electronic environment as on a bulk single crystal surface. A different situation is depicted in Fig. 10.1b. Here, the film is so thin that the buried interface influences the properties of the oxide surface, at least electronically, even if the geometric structure were the same as on a bulk single crystal surface, or, instead, it radically changes structure and properties. These ultrathin films are used to create novel materials or

grow films that are hard to prepare as thicker samples [10.19]. Examples are silica films [10.20-22], aluminosilicate films [10.23], modeling zeolites or films of quasi crystals [10.24]. However, it may also be used to develop and test general concepts by controlling certain parameters via the presence of the oxide-metal support interface. Consider, for example, charge transfer processes. If the energy to remove an electron from the buried oxide-metal interface is smaller than the energy released by attaching this electron to an adsorbate, then this process is favorable and will occur if an appropriate electron transport mechanism is available in the system under consideration [10.25-27]. Such systems may be of interest for studying electron transfer to adsorbed metal nanoparticles, in order to investigate the general influence of electron transfer on the chemistry on supported particles and on the interface between the metal nanoparticle and the oxide film. Another option is to create a film, which does not fully cover the metal support, so that there is an open oxide metal interface between the oxide film and the metal single crystal (Fig. 10.1c) [10.28]. This is often called an inverse catalyst (inverse with respect to metal particles on oxides) which allows the interrogation of the oxide-metal interface [10.29-31]. The nomenclature is, however, somewhat misleading, as it implies that for the interface it does not matter whether one investigates metals on oxides or oxides on metals. Obviously, this is incorrect, because the surface will be different. Still, those investigations may be useful in their own right. A situation, schematically represented in Fig. 10.1c may be encountered when dealing with the so-called strong metal support interaction (SMSI) [10.32-41]. The scenarios sketched in Fig. 10.1b and Fig. 10.1c are, of course, relevant to model catalysts and conceptually such studies also offer the possibility to combine them with approaches modeling the bulk situation based on the scheme depicted in Fig. 10.1a. Figure 10.1d, again, shows an oxide film of sufficient thickness to model the bulk without interference of the buried metal-oxide interface. However, in this case, dopants have been implanted into the oxide film [10.42-48]. If the appropriate combination between host material and dopant is chosen then one might envision that those dopants serve as sources for electron transfer to induce a situation, which is similar to the one encountered for ultra-thin films, described above. Within limits, such an approach may be compared with the standard approach in semiconductor physics, where n- and p-doped semiconductors are used to engineer the band structure and, thus, the electronic properties of those materials [10.49, 50]. Realizing that dopants control the electronic properties of oxides offers yet another possibility for studying ultra-thin films. Imagine the situation depicted in Fig. 10.1e: Here, an ultrathin oxide film is grown homoepitaxially on a specially prepared substrate of the same oxide [10.51-53]. In this substrate oxygen vacancies have been created in the oxide by reduction, which renders the substrate conductive. Given the envisioned homo-epitaxial growth on top, those oxygen vacancies would diffuse into the film grown on top upon thermal treatment. However, if a so-called blocking layer is introduced, the ultrathin film, grown on top will not be influenced by the exchange of vacancies with the underlying substrate and will behave, as if it was grown on a conductive substrate. Yet the entire system would represent a bulk material. This might be a procedure to approach the situation encountered for bulk single crystals, using, however, the advantages of thin film preparations. There is one aspect, which needs to be included conceptually in this introduction. This aspect is concerned with the possibility to remove ultrathin films from their substrate to create truly two-dimensional materials (Fig. 10.1f), similar to graphene [10.54-56], but based on oxides [10.57, 58]. Those films may, of course, be used to create stacks of two-dimensional materials of varying stoichiometry and varying electronic properties [10.59]."

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The paper is organized in four sections: We first report on structural properties of epitaxial oxide films, then we turn to tuning the structural and electronic properties of oxide films, before we discuss their chemical reactivity. While in those sections we report on properties characterized mainly under UHV (ultra-high vacuum) conditions, in the final section we attempt to look at oxide films beyond UHV in an ambient.

#### 10.2 Structural Properties of Epitaxial Oxide Films

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"The number of thin-film model systems that have been prepared and characterized in the past is enormous and covers almost all binary oxides existing in the bulk [10.8, 11, 19, 61]. In fact, the variability of thin-film oxides is even larger than that of their bulk counterparts. The reason can be found in the much higher structural and compositional flexibility of oxide films of few-monolayer thickness, giving rise to a plethora of nonstoichiometric, strained and polar structures that would be unstable in the bulk limit [10.8, 62]. Moreover, the geometric template effect of the substrate combined with different electronic coupling schemes is able to stabilize various unusual thin-film configurations [10.19, 63]. In the following, we will introduce the oxide films explored in our group starting with binary ionic alkaline earth oxide surfaces with simple rock salt structure towards transition metal oxides, which can pose considerable challenges with respect to possible surface terminations. The structural properties provide the necessary basis for the subsequent discussion of the electronic as well as chemical properties discussed in Sect. 10.3 to 10.5.

#### 10.2.1 Mg0 and Ca0(100) Films

The two rocksalt oxides MgO and CaO are probably the most prominent model systems for chemically and catalytically-driven surface science stud-



**Fig. 10.2a–c** Low-temperature STM (scanning tunneling microscopy) images of a 4 ML (monolayer) MgO(100) film on Ag(001), showing an atomically resolved terrace region (**a**), overview and atomically resolved images of a regular step edge (**b**) and an irregular step edge (**c**). Only one ionic sublattice of the MgO is resolved in the measurement. Reproduced with permission from [10.60], © Materials Research Society 2019

ies [10.10]. Their importance relies on several aspects. The rocksalt oxides are characterized by particularly simple structural and electronic properties, i.e., a cubic unit cell with two atoms in the base and a wide, electronic band gap, respectively. As a consequence, they are highly accessible to theoretical calculations, but can also be prepared on a variety of squared atomic lattices with matching dimensions. Suitable supports for MgO (lattice parameter 4.2 Å) are Ag(001) [10.64], Fe(001) [10.65] and Mo(001) [10.66, 67], while CaO (lattice parameter 4.8 Å) is typically grown on Mo(001) [10.68]. Given the symmetry of the support, the rocksalt layers develop their thermodynamically preferred (100) termination that is both structurally compact and charge compensated (Fig. 10.2). Attempts to stabilize alternative rocksalt surfaces, e.g., the (111) termination, turned out to be challenging at least in an UHV environment [10.69]. This can be explained with the polar nature of the hexagonal rocksalt plane, which needs to be compensated for either by surface reconstruction or adsorption of charged adspecies [10.70, 71].

The structural quality of MgO and CaO(100) films is largely governed by a nonperfect lattice match with the support, which induces interfacial lattice strain and needs to be released by structural distortions in the film. Not surprisingly, relatively smooth and homogenous MgO films has been grown on Ag(001) that features only 3° lattice mismatch with bulk MgO (Fig. 10.2) [10.64]. The film quality can be further improved by post-annealing these layers at 773 K, followed by a slow cooling-

down procedure [10.72, 73]. The lattice mismatch due to Mo(001) is considerably larger (5.3°) and results in the development of a dense dislocation network to compensate the strain [10.67]. These line defects share a number of properties with the grain boundaries in realistic, polycrystalline MgO, and shall thus been discussed in more detail [10.74].

The dislocation network has a periodicity of 55-60 Å with straight defect lines running parallel to the MgO[110] direction, as revealed with STM and grazing incidence x-ray diffraction (GIXD) in real and reciprocal space, respectively [10.75]. Along these directions, an extra Mg-O row that has no counterpart in the Mo support is introduced for 18 regular oxide rows. The result is a  $(19 \times 19)$  MgO on  $(18 \times 18)$  Mo coincidence lattice with square symmetry (Fig. 10.3). On the atomic scale, the dislocation network is associated with periodic switches of the interface registry, changing from O to Mg ions sitting atop the Mo atoms of the support. Energetically, the O-Mo registry is preferred, as reflected in a shorter interface binding length (2.3 Å) as compared to the Mg-Mo domains (3.5 Å) [10.76]. As the O-Mo and Mg-Mo regions lie on different height levels, the MgO films develops a considerable mosaicity, being reflected in a prominent splitting of the fundamental MgO spots in low-energy electron diffraction data [10.75]. The modulated interface distance also produces a work function pattern on the MgO film, in which high work function values are found for the Mg-Mo registry, while values for the O-Mo domains are 1.5 eV lower. The differ-



**Fig. 10.3a-d** STM images showing several states of strain relaxation in MgO thin films on a Mo(001) support  $(100 \times 100 \text{ nm}^2, V_S = 4.0 \text{ V})$ . (a) Submonolayer coverage with square shaped MgO islands. Their size is controlled by the interfacial lattice strain. (b) 3 ML thick film displaying a squared coincidence lattice. (c) 7 ML thick film characterized by wide, atomically flat terraces, separated by edge and screw dislocations. (d) 18 ML film with bulk-like lattice parameter. The image quality in (d) is degraded due to the vanishing conductivity of thick MgO layers. Reproduced with permission from [10.60], © Materials Research Society 2019

ence can be explained with the suppressed electron spill-out from the Mo support at the compact O– Mo interface [10.77]. The reduced thermodynamic stability of the Mg–Mo registry finally leads to a higher concentration of point defects in these domains [10.78]. The strain-induced dislocation network on MgO/Mo thin films gives rise to a spatially modulated adsorption behavior that can be exploited as template for the preparation of wellordered ensembles of metal particles [10.76].

With increasing oxide thickness, additional defect types develop next to the dislocation network (Fig. 10.3). Prominent defects at 10 ML film thickness are screw and edge dislocations the latter being aligned with the nonpolar MgO[100] direction [10.75]. Also point defects, in particular oxygen vacancies, become more abundant. They mostly locate along step edges, where the atomic coordination is reduced with respect to atoms embedded in a compact terrace. The lattice position of oxygen vacancies has been thoroughly characterized by angle-dependent EPR (electron paramagnetic resonance) measurements in combination with scanning probe techniques [10.79, 80]."

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Oxygen vacancies can be stabilized in three charge states on the oxide surface that is as neutral ( $F^0$ ), singly ( $F^+$ ) and doubly charged color centers ( $F^{2+}$ ). The latter turned out to be energetically unfavorable in thin films given the quasi infinite electron reservoir of the metal support just below the film. Recent STM and AFM (atomic force microscopy) experiments have proven that the precise charge state of the color centers can be determined on the single-defect level (Fig. 10.4). Whereas STM conductance spectroscopy evaluates the energy position of defect-induced gap states in MgO [10.81], AFM probes the electrostatic interactions between the charged defect and the probe tip [10.82].

Charge trapping is not only observed for point defects, but plays an even larger role for extended line defects in MgO thin films. Several experimental and theoretical evidences have been accumulated that show the enormous ability of line defects to trap excess electrons [10.74]. Quantitative data comes from EPR spectroscopy, where a pronounced bulk-like resonance at g = 2.003 shows up after filling the electron traps by exposure to atomic hydrogen [10.83]. From the disappearance of the signal after annealing to 500 K, the depth of the trap states was estimated to  $\approx 1.0 \text{ eV}$  below the conduction band onset, in good agreement with DFT (density functional theory) models of the MgO grain boundaries [10.84]. Local information on the po-



-2.5V -2.7V -2.8V -3.2V Conductance

**Fig. 10.4 (a,b)** STM images  $(25 \times 25 \text{ nm}^2)$  of a MgO island on 4 ML MgO/Ag(001) imaged at  $V_S = +3.5$  and -3.5 V. (c,d) Continuous scanning of the same surface region at high positive bias produces distinct defects that can be assigned to F<sup>+</sup> (type 1) and F<sup>0</sup> (type 2) color centers. (e) Constant current and conductance images of type 1 defects located at an MgO step edge taken at different bias voltages  $(5 \times 5 \text{ nm}^2)$  [10.81]

sition of the electron traps inside the MgO film comes from STM topographic and luminescence data [10.85]. In high-bias STM images, the MgO line defects appear with negative contrast as compared to the regular film (Fig. 10.5a). As the true geometric corrugation is small, the dark appearance of the dislocations network is interpreted as an electronic effect. In fact, the high number of electrons trapped in the defects leads to a local increase of the electron potential, which in turn reduces the transmissibility for tunneling electrons and forces the STM tip to approach the surface. The shift of the local electron potential due to excess electrons can be quantified by probing the vacuum states above the MgO surface via tunneling spectroscopy [10.86]. The spectra reveal an upshift of the lowest resonance from 3.7 eV on defect-free oxide patches to 4.4 eV above the dislocation lines, in agreement with the anticipated presence of excess charges in the defects [10.83].

Similar information is obtained from STM luminescence maps taken on MgO/Mo films. The oxide's optical response is governed by radiative electron transitions from higher vacuum states to the ground state, and defect-related potential shifts thus produce a contrast in the luminescence pattern (Fig. 10.5b) [10.85]. On regular MgO, the emission channel opens up already at 5.1 V excitation bias and oxide terraces con-



**Fig. 10.5 (a)** STM image of 12 ML MgO/Mo(001)  $(100 \times 100 \text{ nm}^2)$  taken as a function of bias voltage. The line defects appear as deep grooves in the oxide surface as the bias increases. (b) Topographic image and photon maps  $(75 \times 75 \text{ nm}^2)$  taken at the bias position of the second vacuum state on MgO terraces (*middle*) and line defects (*right*). The contrast reversal between both images reflects work function modulations in the film. Reprinted with permission from [10.83]. Copyright (2010) by the American Physical Society

sequently appear bright in those images. Conversely, the optical channel becomes available only at 6.0 V in defect regions, due to the upward shift of the vacuum states, which results in a contrast reversal with respect to the low-bias luminescence maps [10.83].

Charge trapping is a unique behavior of both, point and line defects in MgO thin films. The often weakly bound electrons are susceptible to be transferred into adsorbates, making defects indispensable for the redox chemistry of oxide materials [10.87, 88]. This interrelation has been verified in a number of adsorption and reaction experiments on MgO films, demonstrating for instance low-temperature CO-oxidation over defective MgO/Mo(001) [10.89].

#### 10.2.2 The Silica Film

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"The alkaline earth oxides discussed above represent a class of oxides, which tends to crystallize in a well-defined simple lattice driven by the Madelung potential of the highly ionic system. As discussed above even such prototypical ionic systems exhibit considerable structural complexity in particular with respect to the defect structure. Another level of complexity arises if the system under consideration tends to form amorphous structures.

The prototype for amorphous network structures is silicon dioxide. This material is the simplest and most common type of glass. Many elements and compounds can form glasses and some of the oldest man-made objects found are made from glass materials [10.90–92]. Glass materials and especially silicates are relevant in nature and various branches of modern technologies, e.g., in semiconductor devices, optical fibers and as a support in industrial catalysis [10.93]. In order to push this material class forward and to understand chemical reaction at surfaces in the context of heterogeneous catalysts, we should characterize their structures and properties at the atomic scale.



**Fig. 10.6a–c** Atomically resolved crystalline and vitreous regions of the thin silica film by STM (the scan area of image (a,c) is 3.5 nm × 3.5 nm). Reprinted (adapted) with permission from [10.21]. Copyright (2012) American Chemical Society. An atomic model of the topmost layer of the silica film is superimposed onto the lower section of the images in (a,c) (*green balls*: Si atoms, *red balls*: O atoms). *Zachariasen*'s scheme of crystalline and glass network structures is given in (b) for comparison [10.94]. Reprinted (adapted) with permission from [10.94]. Copyright (1932) American Chemical Society

W.H. Zachariasen postulates laid the foundation to the so-called Random Network Theory 80 years ago to explain the structure of amorphous materials [10.94]. Due to the comparable mechanical properties of amorphous and crystalline materials he assumed that the bonding forces between the atoms in the two phases should be essentially identical. The lack of periodicity and symmetry are the main features that distinguish a glass from a crystal. Early on, it had been suggested that tetrahedral atomic configurations were required to form glasses. Zachariasen used these predictions to sketch an atomic picture of a glass. In his paper he reduced the three-dimensional (3-D) picture into a two dimensions (2-D) analogy (Fig. 10.6b). For silicon dioxide, the simplest structural unit in the 3-D case is a SiO<sub>4</sub> tetrahedron. If the complexity of the system is reduced from 3-D to 2-D, the simplest structural unit for silicon dioxide changes from the SiO<sub>4</sub> tetrahedron to a SiO<sub>3</sub> triangle. The brown circle in Fig. 10.6 marks the SiO<sub>3</sub> building unit. The SiO<sub>3</sub> triangles are linked to each other as individual building blocks at fixed 180° angles, corresponding to a crystalline material. This creates long-range order and periodicity. If the angle between these structural units varies, the building blocks can develop an extended network with rings of different sizes. As can be seen in Fig. 10.6b (bottom) the uniform structural units are linked to each other at apparently random angles. Zachariasen drew a 2-D diagram in which trigonal units are linked together to create the amorphous network. Due to the large variety of Si-O-Si angles which bridge two neighboring building units, the

glass structure lacks periodicity and long range order.

In our department we have developed a recipe to grow thin silica bilayer films on Ru(0001). This film system nicely verifies the complex atomic arrangement of the Random Network Theory with a striking similarity. The observed protrusions at atomic separations in the STM images shown in Fig. 10.6a,c. are arranged in propeller shaped structures. By comparing to Zachariasen's model and based on this propeller symmetry the protrusions can be assigned to Si atoms (green balls in Fig. 10.6a,c). Such propeller shaped units have been separately marked in Fig. 10.6. Here, a Si sensitive contrast is observed and the position of the O atoms has been calculated based on the Si coordinates. In this way the 2-D model of the topmost O and Si atoms has been completed. Please note that a modified tip termination can make the O instead of the Si positions visible [10.21]. This silica film system corroborates crystalline structures [10.20], but also verifies Zachariasen's predictions of a vitreous random network for a glass [10.22].

Besides the separate characterization of each phase, also interface structures between crystalline and amorphous phases have been addressed [10.95]. In the glass community, there has always been a controversy about how crystalline and vitreous phases are connected to one another. From the experimental point of view, a real-time observation at the atomic scale of an active front during a glass transition process is not currently feasible. But a static image of such an interface region can be gained. For further details see [10.95].



Fig. 10.7a-c Models of iron oxides structure for (a) wustite (FeO), (b) magnetite ( $Fe_3O_4$ ), and (c) hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>)

Furthermore, it should be mentioned that silica bilayer films can be grown on a number of substrates [10.22, 96–98], which leaves room for tuning the properties of these films, but also shows that these films resemble a completely new materials class of its own.

With these experiments, a clear image of an amorphous material has been obtained which allowed for the first time the derivation of atomic sites and a detailed analysis from real space coordinates. The text book example of the amorphous silica structure proposed by Zachariasen in 1932 has thereby finally been verified. Also Mo(112) and Pt(111) substrates have been used to prepare thin silica films.

#### 10.2.3 Iron Oxide Films

The oxide films discussed so far were simple in the sense that the oxidation state of the constituents is well-defined. This restriction is lifted if transition metal oxides are considered. In addition, the ability to form oxides with different formal oxidation states of the metal ion is associated with changes in the bulk crystal structures. With respect to the atomic structure of the surfaces observed for different oxides the surface termination becomes a central aspect. To illustrate these aspects we will present results on iron oxide films.

Iron oxides films have a wide field of technological applications, ranging from magnetic devices to heterogeneous catalysis [10.99, 100]. This class of material exhibits rather different magnetic or conducting properties [10.101] depending on their crystal structures, which is strongly determined by the way of preparation. The morphology and termination of the oxide film have a strong influence on the chemical properties and are, therefore, subject of intense studies [10.102-105]."

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Figure 10.7 briefly sketches the crystal structures of iron oxide phases discussed in the following, the main ones being FeO (wustite), Fe<sub>3</sub>O<sub>4</sub> (magnetite) and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (hematite). For a more detailed overview of these different crystalline structures see Weiss and Ranke [10.102]  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> crystallizes in the corundum structure with a hexagonal unit cell. Along the [0001] direction the O anions form a close-packed hcp sublattice with ABAB stacking. The Fe<sup>3+</sup> species between these layers are arranged in honeycomb  $(\sqrt{3} \times \sqrt{3})$ R30° like layers. Fe<sub>3</sub>O<sub>4</sub> crystallizes in the inverse spinel structure. The O anions form a close-packed fcc sublattice (ABC stacking along the [111] axis of the lattice) with  $Fe^{2+}$  and  $Fe^{3+}$  cations located in the interstitial sites. The O planes are similar to those in α-Fe<sub>2</sub>O<sub>3</sub>. Between the close-packed planes of oxygen ions either one Kagomé or three hexagonal (mixtrigonal) Fe layers alternate. Both ion sublattices are arranged in a  $(2 \times 2)$  like fashion on the close-packed oxygen layer. FeO crystallizes in the rock salt structure, hence the O and Fe (111) planes form ideal two-dimensional hexagonal lattices with a cubic ABC stacking sequence along the [111] direction. FeO films in (111) termination are intrinsically unstable as they develop a polar dipole that increases with film thickness. The impact of the polarity on the



**Fig. 10.8a,b** Morphology of a well-prepared  $Fe_3O_4$  film, completely covering the Pt(111) support. Both LEEM images show the identical surface area in (a) bright- and (b) dark-field imaging mode, utilizing the (0;0) and the (1/2;0) diffraction spots, respectively. The contrast is caused by the morphology. Additionally, domains rotated by 180° become visible as dark areas in the dark-field image. Reprinted with permission from [10.106]. Copyright (2012) by the American Physical Society

local surface potential largely governs the adsorption behavior of the film, and can be probed with STM, for example [10.107].

#### Morphology of Thin $Fe_3O_4(111)$ Films

Fe<sub>3</sub>O<sub>4</sub>(111) films of about 10 nm thickness were grown on a Pt(111) single crystal support by repeated cycles of Fe deposition at room temperature (RT) and oxidation at elevated temperatures, after one complete FeO layer was formed initially [10.102]. In each cycle, between 5 and 10 ML of Fe was deposited, and oxidized at  $1 \times 10^{-6}$  mbar of O<sub>2</sub>, starting at RT, followed by annealing to 900 K, which was kept for 5 min. Upon cooling, the oxygen pressure was reduced only after cooling to 500 K. By following this procedure, the Pt(111) crystal is completely covered by an  $Fe_3O_4$  film (Fig. 10.8a). The LEED (low energy electron diffraction) pattern of the film matches perfectly the one described in literature [10.108]. The film consists of terraces up to a width of 100 nm, most of them with polygonal shape. As seen in LEEM (low energy electron microscopy), the step density increased after every cycle, especially  $> 20 \,\mathrm{nm}$  of film thickness. However, the film could be smoothed if the final oxidation treatment was done at an elevated temperature of  $\approx 1000$  K. Here, it was necessary that the film was completely closed and thicker than 7 nm, otherwise the annealing up to 1000 K led to a de-wetting (see the following section). A subsequent thermal flash in UHV did not produce further morphological changes, but improved the homogeneity of the surface structure (see Sect. 10.2.3).

Magnetite crystallizes in an inverse spinel structure with space group Fd3m, while the Pt substrate exhibits a fcc structure with space group Fm3m. Therefore, the Fe<sub>3</sub>O<sub>4</sub>

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"islands created by initial nucleation on a clean Pt(111) surface may coalesce with improper stacking [10.109, 110] and form a complete film with two twin domains rotated by 180°. Dark field LEEM studies using the (1/2;0) and (0;1/2) spots showed a predominance of one rotational domain; coverage ratio for these rotational domains ranged between  $75^{\circ}/25^{\circ}$  and  $98^{\circ}/2^{\circ}$ , depending on the preparation condition. Figure 10.8b shows a darkfield LEEM image visualizing the two rotational domains as dominating bright and small black areas. This preponderance is maintained even after subsequent cycles of Fe deposition and oxidation. On average, the rotational domain size is larger than the terrace width; some of the domains were even several µm wide. A comparison between dark field and bright field LEEM images shows that the rotational domains are preferentially placed in correspondence of the step bunches of the substrate, providing a partial correlation be-



**Fig. 10.9a–f** Dewetted  $Fe_3O_4$  film, studied by (a) LEED, (b–e) LEEM and (f) XPEEM. The LEED pattern shows a superposition of the  $Fe_3O_4$  and FeO structures. The LEEM images use selected LEED spots as labelled in (a). In the bright-field LEEM image (b) the  $Fe_3O_4$  and FeO surface areas appear dark and bright, respectively. The dark-field images (c,d) identify the  $Fe_3O_4$  area with rotational domains, whereas in (e) only the FeO layer appears bright. (f) XPEEM image using the Pt  $4f_{7/2}$  photoemission line. Adapted from [10.106]

tween substrate morphology and crystallographic inhomogeneities."

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#### Morphological Inhomogeneities

The oxidation temperature plays a crucial role for the uniformity of the thin film.

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"On the one hand it should be high enough to enable the oxidation process, but on the other hand not too high, especially during the first deposition cycles, to avoid a de-wetting of the Fe<sub>3</sub>O<sub>4</sub> film. The latter was observed for a film thickness of 7 nm at oxidation temperatures above 900 K, as FeO areas became clearly visible in the *holes* of the Fe<sub>3</sub>O<sub>4</sub>(111) film. The width of these FeO domains increased dramatically at further increase of the temperature, from

approximately 100 nm to several µm for an oxidation temperature of 1000 K. The FeO areas could be identified by various experiments: bright and dark field LEEM (Fig. 10.9b-e), LEED (Fig. 10.9a) and XPEEM (x-ray photoelectron emission microscopy) (Fig. 10.9f). In the de-wetted case bright field LEEM images (Fig. 10.9b), Fe<sub>3</sub>O<sub>4</sub> (dark) and FeO (white) areas are visible with different contrast, while the corresponding LEED pattern shows the superposition of the  $Fe_3O_4(111)$  pattern and the Moiré pattern (six satellite spots surrounding the central (0;0) spot) typical for the FeO(111)/Pt(111)interface. By dark field imaging using the Fe<sub>3</sub>O<sub>4</sub> (1/2;0) and (0;1/2) spots (Fig. 10.9c,d) the FeO areas appear dark, while the  $Fe_3O_4$  areas show a contrast between rotational domains due to the threefold symmetry of the  $Fe_3O_4(111)$  crystal structure. On the contrary, the FeO domains can be unambiguously identified as brighter areas if one of the satellite spots around (0;0) is selected (Fig. 10.9e). XPEEM images obtained with Pt 4f7/2 core level emission line (Fig. 10.9f) additionally reveal that the FeO domains formed by de-wetting are indeed deep holes in the  $Fe_3O_4$  film."

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The FeO areas are so thin that the electrons photoemitted in the Pt substrate can still pass through, while the Fe<sub>3</sub>O<sub>4</sub> film is thick enough to completely damp the Pt signal. Considering the electron mean free path length of  $\approx 0.5$  nm at the used kinetic electron energy (104.2 eV), one can estimate the thickness of the FeO areas as a few Angstroms. Once the Fe<sub>3</sub>O<sub>4</sub> film had de-wetted and FeO holes were formed, it was not possible to recover a closed  $Fe_3O_4$  film by several additional cycles of Fe deposition and oxidation. Obviously, the Fe atoms adsorbed on the FeO areas at room temperature migrated onto the Fe<sub>3</sub>O<sub>4</sub> areas during the oxidation process at 900 K. Consequently, only the Fe<sub>3</sub>O<sub>4</sub> grew in thickness, while the FeO zones remained unchanged. Furthermore, wide-range LEEM images of an almost closed Fe<sub>3</sub>O<sub>4</sub> film show that FeO domains are formed preferentially at the step bunches of the Pt(111) substrate, where the  $Fe_3O_4$  is unstable, most likely due to the strain induced by the steps and step bunches [10.106].

#### Surface Termination

Besides the two inhomogenities in the rotational domains and in the morphology, a third type related to the surface termination was found and was investigated using four techniques:

- SPALEED (spot profile analysis low energy electron diffraction (profile analysis of LEED spots)) studying the profile of the LEED spots in-real-time during oxidation and flash in UHV yielding the domain sizes for different preparations
- (ii) XPS (x-ray photoelectron spectroscopy) of the surface before and after the final annealing, determining the chemical composition of the surface, excluding contaminations of carbon, nitrogen or molybdenum containing species
- (iii) STM of the *as prepared* surface, visualizing about 2 nm wide objects and therefore smaller than the LEEM resolution
- (iv) Dynamical LEED analysis of the spot intensities for differently prepared surfaces, studying the surface unit cell structure and therefore the termination [10.106].

In the special LEEM set-up, we collected *I/V*-LEED (intensity/voltage low energy electron diffraction (in-

tensity analysis of LEED spots)) spectra of the Fe<sub>3</sub>O<sub>4</sub> thin film at room temperature before and after the flash at 900 K. The intensity of six different diffraction spots, (0;0), (1/2;0), (0;1/2), (1;0), (0;1) and (1/2;1/2), were analyzed within an energy range between 40 and 300 eV, equivalent to an overall dataset of 1560 eV. In contrast to a standard back-view LEED, the operation condition of the electron gun and the image columns of our system are not altered during the energy scan, but solely the sample potential is changed. Consequently, the beam current on the sample is constant during the scan, for all experiments. Additionally, due to the special LEEM optics the investigated diffraction spots do not move in position on the detector during the energy scan and the (0;0) spot is visible even at full perpendicular illumination. It is also possible to directly inspect the probed surface region from where the diffracted electrons are collected. Combining this with a dark field image, which gives the portions of the two possible rotational domains, one can easily disentangle the contributions of the two rotational domains and extract the real spectra of (1/2;0), (0;1/2), (1;0) and (0;1)spots of a single rotational domain. This is not possible with a standard back-view LEED set-up because of the superposition of two threefold pattern with unknown relative abundance. Therefore, one is usually forced to average the spectra of spots of the same diffraction order, with consequent loss of information.

The resulting disentangled I/V-LEED spectra for the as prepared and after flash surfaces differ strongly in some energy ranges (see arrows in Fig. 10.10). This can be interpreted as a change in the surface termination. Additionally, we found that the spectra of the as prepared surface do not change significantly for different cooling rates. For a full I/V-LEED analysis different models for the surface atomic structure were assumed, from simple truncation of the bulk crystal unit cell along the (111) plane, yielding six different terminations, up to more complex structure models, i.e., with incomplete site occupation and/or changed coordination sites. Every configuration was optimized until the change in each atomic coordinate in a single iteration loop was < 0.1 Å. The most reliable model with a resulting Pendry reliability (R) factor of R =0.14 is 1/4 ML Fe atom belonging to the MixTrigonal layer on a closed-packed oxygen layer resting upon a Kagomé iron layer. The surface after the flash presents the expected atomic termination and confirms the results obtained first by Barbieri et al. [10.104] and then by *Ritter* and *Weiss* [10.111].

The fit of the I/V curves measured for *as prepared* films gave no clear resulting structure because all *R*-factors were much larger with respect to the values obtained for the flashed surface. The most reliable model



Fig. 10.10 Surface termination of the Fe<sub>3</sub>O<sub>4</sub> films at different preparation steps. IV-LEED curves of the first six diffraction spots for the asprepared film (in blue) and after annealing at 900 K in UHV (in red). The major changes due to this flash are indicated by arrows. Reprinted with permission from [10.106]. Copyright (2012) by the American Physical Society

was still the one described above for the flashed surface, but with a *R*-factor of 0.33 much worse than before. One can assume that, as shown by STM, part of the *as prepared* surface exposes the termination dominant after the annealing. Therefore, the spectra were also fitted with a linear combination of the *after flash* surface and the unknown structure. Even with this extra parameter, the analysis did not result in structures with acceptable *R*-factor. Simple explanations, that the IV-LEED method fails in this case, are (i) the low atomic order of the objects, as seen in STM, and (ii) the small object size of 2 nm (i.e.,  $\approx$  7 atomic distances), not suitable for the method, which assumes infinite periodic conditions. The nature and the origin of these *extra objects* could be studied indirectly. In the (0;0) LEED spot profiles they exhibit a significant shoulder like broadening, corresponding to an average domain size of 2 nm, as also observed in STM. Real time SPALEED measurements clearly show, that the extra objects were not present during the oxidation process at temperatures > 900 K, but were formed during the cooling down at temperatures < 750 K. Furthermore, if the oxygen exposure was cut off during the cooling process > 750 K, no extra object was detected. Therefore, the formation of extra objects on the surface must be directly related to the O<sub>2</sub> exposure at lower temperature. Once formed, the extra objects can be completely removed by annealing up to 900 K in UHV. As shown in LEEM and SPALEED, this flash in UHV transforms the *as prepared* surface with a rough morphology and small objects of less-ordered and highly oxygen containing domains into a smooth surface with a homogeneous 1/4Fe termination. Therefore, this final flash determines the morphology and termination of the prepared Fe<sub>3</sub>O<sub>4</sub> film. Recent studies indicate that the extra objects may be due to water adsorption from the background.

## Interconversion of Fe $_30_4$ (111) and $\alpha$ -Fe $_20_3$ (111) Thin Films

An additional inhomogeneity observed in oxide films are domains of different bulk structures. Under our preparation conditions iron oxide films grown on the Pt(111) or Ag(111) surfaces were composed of the Fe<sub>3</sub>O<sub>4</sub> phase and of a few microns large domains of α- $Fe_2O_3$ , covering a few percent of the entire surface. The two phases coexist for intermediate preparation parameters [10.112], often also showing small FeO domains due to partial dewetting (Fig. 10.11a). The annealing of the film in  $3 \times 10^{-5}$  mbar O<sub>2</sub> pressure (i.e., a higher pressure than used for the initial preparation) starting at RT up to 700 K, leads to an oxidation of the Fe<sub>3</sub>O<sub>4</sub> area into  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> as monitored in LEEM (Fig. 10.11b-i). The conversion starts at 670 K (Fig. 10.11c) as a growth front of dendritical shape. The process becomes faster when the temperature is increased, indicating that the transformation process is thermally activated [10.113].

The conversion can be inverted by extra Fe deposition, which leads to a shrinkage of the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> upon annealing in UHV. Here, the Fe is incorporated into the hematite area, causing a change in stoichiometry and crystal structure [10.112]. Without Fe deposition, annealing in UHV can also lead to a reduction of the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> by desorption of oxygen. This was observed when Ag(111) was used as support [10.112, 114]. However, on a Pt(111) support, the UHV annealing yields the opposite result: the  $Fe_3O_4$  is converted into  $\alpha$ - $Fe_2O_3$ . The reason for this unexpected behavior is the special ability of the Pt(111) support to dissolve Fe. Therefore, Fe from the  $Fe_3O_4$  phase can diffuse into the bulk, producing an intermediate nonstoichiometric Fe<sub>3</sub>O<sub>4</sub> phase or even  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, which subsequently is structurally transformed into hematite.

The preparation of  $\approx 10$  nm thin iron oxide films on metal supports is determined by various parameters like growth temperature, oxidation temperature and pressure but also kind and morphology of the supporting substrate. These parameters may have a crucial influence on e.g., the film morphology, the film roughness, surface termination and crystal structures. Therefore, the control of the preparation is essential for the proper characterization of the chemical properties of oxide films.

#### 10.2.4 Other Transition Metal Oxide Surfaces

#### Surface Structure of $V_2O_5(001)$ and $V_2O_3(0001)$

Vanadium oxides are catalytically active for a number of reactions, most of them involve the transfer of oxygen atoms [10.115] which triggered a number of studies in the areas of basic and applied research. Some aspects are summed up in recent review papers [10.14, 62, 116–120]. Vanadium catalysts are often based on V<sup>5+</sup> but lower oxidation states are likely to play a role during catalytic processes. The relevance of vanadium oxides in catalysis has motivated scientists to perform model catalytic studies for which well-characterized high-quality crystalline oxide surfaces are required.

Ordered  $V_2O_5(001)$  layers have been prepared on Au(111) only [10.121, 122], while  $V_2O_3(0001)$  layers have been grown on a number of substrates: Au(111) [10.123, 124], W(110) [10.125], Rh(111) [10.126], Pd(111) [10.127], and Cu\_3Au(100) [10.128]. There have also been reports of VO<sub>2</sub>(110) growth on TiO<sub>2</sub>(110) [10.129] and SnO<sub>2</sub>(110) [10.130, 131] but extended adsorption/reaction studies have not been reported.

The main difference between the preparation recipes for  $V_2O_5(001)$  and  $V_2O_3(0001)$  is that the preparation of  $V_2O_5(001)$  layers requires higher oxygen pressures than the preparation of  $V_2O_3(0001)$  layers: the former is prepared in an oxygen pressure in the 50 mbar range [10.121, 122] while for the latter UHV compatible pressures in the  $10^{-6}$  mbar range suffice [10.123–125]. The preparation recipe for  $V_2O_5(001)$  on Au(111) is described in detail in [10.122]: well defined layers with a very low density of point defects may be produced as shown in Fig. 10.12. The bonding of the  $V_2O_5(001)$ layers to the Au(111) substrate is so weak that the islands in in the left panel of Fig. 10.12 exhibit different azimuthal lattice directions which leads to ring-type intensity patterns in the LEED images [10.122]. When enough material is deposited to close the layers then the islands grow together which leads to the lines in the center panel where azimuthally differently oriented areas meet.  $V_2O_5(001)$  is terminated with vanadyl double rows which are clearly recognizable in the right panel of Fig. 10.12.

 $V_2O_3(0001)$  layers may also be grown on Au(111) [10.123–125]. These layers are also well ordered but with a somewhat higher density of point defects, see Fig. 10.13. The surface structure of a model



 $p_{O_2} = 3 \times 10^{-5} \text{ mbar}$ in a temperature range between RT and 700 K. Images are taken in the sequence from (a) to (i) whereas the conversion time and temperature are indicated at the respective image. (a) The initial surface consists of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (*dark*) and Fe<sub>3</sub>O<sub>4</sub> (*bright*) areas and FeO holes (bright). Between (f) and (g) the sample was shifted to follow the conversion front. As a help for the eye, the *circle* marks the identical surface spot. Reprinted (adapted) with permission from [10.112]. Copyright (2014) American Chemical Society

460 s, 695 K

catalyst is a relevant parameter for its catalytic activity and therefore this aspect was investigated in detail in the first stages of the  $V_2O_3(0001)$  related studies.

 $V_2O_3$  has a corundum lattice and the (0001) surface is a basal plane of this hexagonal lattice. Seen from the side, this lattice consists of alternating quasihexagonal oxygen layers and vanadium double layers. Three different surface terminations may be obtained by cutting the structure parallel to (0001): DM, SM, and bulk O<sub>3</sub>, see Fig. 10.14. The stability of such surfaces from an electrostatic point of view has been initially analyzed by Tasker [10.133] who could show that polar structures, i.e., structures with electrically

nonneutral layers parallel to the surface may energetically be stable only under certain conditions. The consequences have been discussed for a large variety of systems and the interested reader may be referred to the current literature [10.8, 70] Among the V<sub>2</sub>O<sub>3</sub> terminations shown in Fig. 10.14 only SM is electrostatically stable according to the *Tasker* criteria [10.133]. However, the vanadium atoms at the SM terminated surface are chemically rather active and therefore it was assumed that the surface might actually be terminated by vanadyl groups, V=O in Fig. 10.14. This assumption was later supported by infrared spectroscopy and HREELS (high resolution electron energy loss spec-



Fig. 10.12a-c STM images of  $V_2O_5(001)/Au(111)$ . (a)  $V_2O_5(001)$  islands on Au(111),  $100 \times 100 \text{ nm}^2$ , U = 3 V, I = 0.2 nA. (b) Closed  $V_2O_5(001)$  layer,  $50 \times 50 \text{ nm}^2$ , U = 2 V, I = 0.2 nA. (c) Small area scan,  $5.8 \times 6.4 \text{ nm}^2$ , U = 3.5 V, I = 0.2 nA. For details see [10.121, 121]



Fig. 10.13 STM image of vanadyl terminated  $V_2O_3(0001)$ on Au(111),  $20 \times 20 \text{ nm}^2$ , U = 1.5 V, I = 0.2 nA. After [10.132]

troscopy) data which feature intense structures related to the vanadyl V=O vibration and by STM data like the one shown in Fig. 10.13 [10.125, 126]. This model was later challenged by studies featuring ion scattering experiments and DFT calculations which came to the conclusion that the surface termination should be the one named rec. O<sub>3</sub> in Fig. 10.14 [10.127, 134, 135]. This structure is similar to the bulk O<sub>3</sub> termination with the difference that a vanadium atom from the second double layer below the surface moves into the first vanadium double layer below the surface. This view was recently refuted by a detailed combined I/V-LEED + STM + ion scattering study which could conclusively show that the surface is terminated by vanadyl groups under standard UHV conditions [10.123, 124].

#### Preparation of Rutile $TiO_2(110)$ Layers on Rutile $TiO_2(110)$ Single Crystals with a Diffusion Blocking Layer

Mixed or doped oxides may offer additional catalytic reaction paths due to the presence of the additional component which may play a role for a specific reaction. This issue was studied with the example of vanadium mixed into rutile  $TiO_2(110)$ . The first step of that project was the preparation of a suitable sample. Several tries were made to prepare ordered  $TiO_2(110)$  layers on different gold and platinum surfaces but suitable layers could not be obtained (see Sedona et al. [10.136] for  $TiO_x$  on Pt(111)). Interface stress due to overlayer-substrate lattice mismatch was assumed to be the reason for this failure and therefore it was tried to prepare  $TiO_2(110)$  layers on rutile  $TiO_2(110)$  single crystals [10.51] since in this case the lattice parameters of the overlayer and the substrate would be identical. High-quality layers could be prepared in this way, but when vanadium was mixed into the layers it turned out that the vanadium diffused into the substrate at temperatures required for the preparation of the films, so that vanadium doped oxide layers could not be prepared. In the next step a layer between the overlayer and the substrate was introduced with the aim of blocking vanadium diffusion. The blocking layer was a  $TiO_2(110)$ layer with ions of another metal mixed into it. The admixed metal was chosen such that the ionic diameter of its 4+ ions was somewhat larger than that of the Ti<sup>4+</sup>



Fig. 10.14 Different possible  $V_2O_3(0001)$  surface terminations (DM: double metal termination; SM: single metal termination). For details see text. *Brown*: bulk oxygen, *beige*: vanadyl oxygen, *gray*: vanadium. Reprinted (adapted) with permission from [10.123]. Copyright (2015) American Chemical Society

ions in  $TiO_2(110)$ . This stresses the rutile lattice of the TiO<sub>2</sub> host oxide, thereby increasing the diffusion barrier. A relevant property of the blocking layer is that it is a good support for the growth of rutile  $TiO_2(110)$  overlayers, with and without vanadium doping. Therefore the structure and the lattice parameters of the blocking layer had to be very similar to the corresponding rutile TiO<sub>2</sub> properties. For this reason the metal ions mixed into the blocking layer were chosen among metals having oxides with rutile structure. Another relevant property is the thermal stability with respect to diffusion of the admixed metal ions, which should be high to prevent diffusion of the admixed ions into the overlayer and finally to the surface. Lead, tungsten and tantalum were tested as admixed components in the blocking layer. Lead appeared to segregate and was therefore discarded. Tungsten ions turned out to be thermally less stable than tantalum ions and therefore tantalum was selected to be the metal admixed to the TiO<sub>2</sub> in the blocking layer [10.51]. The prepared blocking layers were usually  $\approx$  3 nm thick and had an approximate composition of  $Ti_{0.8}Ta_{0.2}O_2$ . The thermal stability of the layers was such that with XPS weak tantalum signals could only be detected in surface-near regions of the top layer after 10 h of annealing at 800 K or 2 h at 900 K.

It was demonstrated that the blocking layer does not only impede vanadium diffusion but also the diffusion of Ti<sup>3+</sup> ions resulting from the reduction of TiO<sub>2</sub>(110) [10.51]. This is illustrated in Fig. 10.15 which shows UPS (ultra-violet photoelectron spectroscopy) spectra of the  $TiO_2(110)$  band gap state which is known to be related to  $Ti^{3+}$  ions [10.137–139]. The spectra have been measured at a grazing electron detection angle which means that most of the intensity in the spectra stems from just the topmost layer of the respective sample. Spectrum (b) was recorded from a sputtered single crystal after annealing at 800 K in vacuum for 10 min while spectrum (d) is the spectrum of a  $TiO_2(110)$  layer subjected to the same procedure. Both, sputtering and annealing produce Ti<sup>3+</sup> ions. However, the Ti<sup>3+</sup> related feature at  $\approx 0.75 \text{ eV}$  is much



**Fig. 10.15** HeI UPS spectra of differently prepared TiO<sub>2</sub>(110) surfaces recorded at an electron detection angle of 70° with respect to the crystal surface normal. The spectra show the energy range of the TiO<sub>2</sub>(110) band gap region. (*a*) Single crystal annealed at 800 K in  $10^{-6}$  mbar O<sub>2</sub> for 10 min. (*b*) Single crystal reduced by sputtering at RT and annealing at 800 K in vacuum for 10 min. (*c*) TiO<sub>2</sub>(110) thin film annealed at 800 K in  $10^{-6}$  mbar O<sub>2</sub> for 10 min. (*d*) TiO<sub>2</sub>(110) thin film reduced by sputtering at RT and annealing at 800 K in vacuum for 10 min. (*e*) The layer produced in step (*d*) annealed for 10 more min at 800 K in vacuum. Reprinted (adapted) with permission from [10.51]. Copyright (2016) American Chemical Society



**Fig. 10.16a–c** STM images (2.0 V, 0.1 nA) of differently prepared TiO<sub>2</sub>(110) surfaces. (a) A TiO<sub>2</sub>(110) thin film annealed in vacuum at 900 K for 20 min. (b) A TiO<sub>2</sub>(110) thin film annealed in 10<sup>-6</sup> mbar O<sub>2</sub> at 600 K for 10 min. (c) A TiO<sub>2</sub>(110) single crystal surface annealed in 10<sup>-6</sup> mbar O<sub>2</sub> at 600 K for 10 min. For the images shown in (b,c) the samples were annealed at 800 K in vacuum prior to oxidation which resulted in flat surfaces with large terraces. Reprinted (adapted) with permission from [10.51]. Copyright (2016) American Chemical Society

more intense in the spectrum of the thin film. This would not be the case if the  $Ti^{3+}$  ions could pass the blocking layer since in this case the  $Ti^{3+}$  ions would have diffused into the substrate, which happened in the case of the single crystal substrate (spectrum (b)) and led to the smaller intensity in the spectrum. Further annealing of the thin film did not change the intensity of the band gap state since the  $Ti^{3+}$  ions could not diffuse into the substrate (spectrum (e)).

TiO<sub>2</sub>(110) single crystals studied with electrons (using electron spectroscopy, electron scattering, STM, ...) have to be electrically conductive which is usually achieved by a mild reduction which produces  $Ti^{3+}$  ions. In addition to vacancies in the bulk this leads to oxygen vacancies at the surface (*bridging oxygen vacancies*) which may and often do play a role in catalytic surface reactions. The introduction of blocking layers offers a way to prepare surfaces without bridging oxygen vacancies which do not charge and can therefore be studied with charged particles, provided that the layers are not too thick. Also strongly reduced layers may be prepared without reducing the substrate notably.

Figure 10.16a displays a STM image of a  $TiO_2(110)$ film ( $\approx 10$  nm thick, on a blocking layer) after annealing in vacuum. A high density of bridging oxygen vacancies (the links between the continuous rows) is observed as expected from the discussion above. After annealing in oxygen (Fig. 10.16b) the bridging oxygen vacancies are not visible anymore and some bright features on the rows show up, which are attributed to oxygen adatoms, resulting from oxygen dissociation [10.138, 140]. The result is different if the single crystal is exposed to oxygen (Fig. 10.16c). In this case extended structures form which result from the diffusion of Ti<sup>3+</sup> ions to the surface where they are oxidized [10.141]. Since there is no blocking layer in the case of the single crystal, Ti<sup>3+</sup> ions from far below the surface can diffuse to the surface which the reason for the formation of the extended protrusion in Fig. 10.16c.

It could be shown that vanadium admixed to  $TiO_2(110)$  prefers subsurface locations under reducing conditions [10.53]. The vanadium has the effect that the host oxide becomes more reducible, which was traced back to the lower binding energy of vanadium to oxygen [10.53]. This has the effect that layers containing vanadium are usually more reduced than layers without vanadium, which affects the surface reactivity: bridging oxygen vacancies and extended reduction induced defects like the strands known for heavily reduced (1 × 2) reconstructed  $TiO_2(110)$  appear in elevated concentrations at the surface, where they may interact with adsorbates, modifying reactions rates, selectivities and reaction paths.

#### 10.3 Tuning the Properties of Oxide Films

Apart from the structural properties of oxide films, which have been addressed in the previous section, it is important to elucidate the physical and chemical properties of these systems in more detail. Within this section we would like to elucidate the possibilities to tune the properties of the oxide films. A variety of strategies have been reported in literature on how the properties of these systems can be modified. We will



Fig. 10.17 (a) STM image  $(30 \text{ nm} \times 30 \text{ nm})$  of Au atoms adsorbed on a 3 ML thin MgO film. (b) Experimental STM image and (c) calculated STM image of Au atoms on 3 ML MgO/Ag(001). (d) STM image  $(5 \text{ nm} \times 5 \text{ nm})$  of Au atoms on 3 ML MgO/Ag(001); the *grey lattice* is the ionic sublattice extracted from a high resolution image of the clean MgO film

restrict the discussion to two aspects. First we would like to discuss the effect of film thickness. We will refrain from discussing the complex structural variability of several ultrathin oxide film systems, which have been reviewed recently, but we will focus on charge transfer processes and their impact on the properties of molecular adsorbates as well as metal atoms and particles. While a discussion of ultrathin oxide films may sound like an academic curiosity it is important to note that the concepts observed for the ultrathin films can largely be transferred to bulk oxides if suitable electron donors or acceptors are provided. We will use CaO as an exploratory example to show how suitable doping of a bulk, wide-band gap oxide can modify the properties of the system, which is very comparable to the observations made for the ultrathin MgO film.

#### 10.3.1 Charge Transfer Effects on Thin Oxide Films

MgO as the prototype of an ionic oxide is a good starting point for the discussion of charge transfer effects on thin oxide films. The interaction of molecules as well as metal atoms with the stoichiometric (001)-plane of the rock salt lattice is rather weak resulting in a low stability of individual metal atoms and growth of 3-dimensional metal particles at ambient temperature. Gold atoms adsorbed on bulk like 30 ML MgO(001) films were shown to be neutral entities [10.142]. However, the binding of the atoms on-top of the oxygen ions of the MgO lattice leads to a polarization of the valence electrons of the Au atom, which enables charge transfer to molecular adsorbates such as CO [10.143]. Theory had proposed that Au atoms deposited onto ultrathin MgO films get negatively charged due to a charge transfer from the metal substrate to the Au atom [10.25, 144, 145]. This is due to the fact that the unoccupied part of the Au 6 s level found in the band gap on thick films is located below the Fermi-energy of the support for the thin film system. There are different contributions to this effect. First, the deposition of MgO onto the metal substrate reduces the work function of the system, which has been confirmed both theoretically as well as experimentally [10.64, 77, 146]. Second, charged Au atoms adsorbed on the surface of the ultrathin MgO film are stabilized by polaronic distortions of the oxide lattice [10.144, 147].

Experimental evidence for the charging of Au atoms on ultrathin MgO(001) films comes from low-temperature STM experiments. As seen from the STM image (Fig. 10.17a) Au atoms deposited on a 3 ML MgO film (T = 5 - 10 K) form an ordered structure indicating significant repulsion between them [10.27]. In contrast to that adsorption of Pd atoms (3 ML thick MgO film, T = 5 - 10 K) is in perfect agreement with expectations based on a statistical distribution of the atoms [10.27]. Further evidence for a charged state of the Au atoms can be found from the STM signatures of single Au in comparison with simulated ones applying the Tersoff-Hamann approximation (Fig. 10.17b,c) [10.149]. The experimental appearance of the Au atoms showing a sombrerolike protrusion surrounded by a depression is nicely reproduced theoretically, however, it is absent in the simulated STM images of neutral atoms [10.150]. Similar observations were found for other systems such as Au on ultrathin NaCl films [10.151]. To elucidate this question in more detail it is interesting to note that on bulk MgO or thick films Au atoms were found to nucleate on top of oxygen ions [10.142], while theory predicts charged Au atoms on thin films to adsorb preferably on Mg sites or hollow sites [10.25, 144, 152]. STM can provide evidence for the change in the distribution of the adsorption sites by superimposing the



**Fig. 10.18** (a) EPR spectrum of  $20 \text{ L O}_2$  adsorbed at 40 K on a 4 ML thick MgO(001) film on Mo(001) with the magnetic field in the surface plane along a [110] equivalent direction. (b) Result of a DFT calculation of O<sub>2</sub> on a 2 ML thin MgO(001) film on Mo(001) showing the polaronic distortion of the MgO lattice. (c) Sketch of oxygen molecules adsorbed on 2 ML MgO films as predicted by theory. The *transparent area* indicates the plane in which the magnetic field was lying in (a). The orientation of the three principal components of the *g*-matrix of the two symmetry equivalent molecules are shown as *color coded arrows*. As an EPR experiment probes the *g*-value oriented along the static magnetic field it is readily clear that both molecules are not identical for the magnetic field lying in the surface plane. Adapted from [10.148]

MgO lattice on the STM images of Au atoms. For an 8 ML film > 80% of the atoms occupy one adsorption site, while at least two different adsorption sites are populated with almost equal probability on 3 ML films (Fig. 10.17d), which clearly shows the change in adsorption site [10.27].

Charge transfer is not restricted to metal atoms with sufficiently high electron affinity, but was theoretically predicted for molecules with high electron affinities such as NO<sub>2</sub> or O<sub>2</sub> adsorbed on ultrathin MgO(001) films grown on Ag(001) or Mo(001) [10.147, 153, 154]. From an experimental point of view the characterization of the superoxide anion  $(O_2^-)$  can be approached using EPR spectroscopy [10.155] as the superoxide anion is a radical with a doublet ground state. Figure 10.18a shows an EPR spectrum of molecular oxygen adsorbed at 40 K on a 4 ML thick MgO(001) film grown on Mo(001) [10.148]. The spectrum consists of a doublet of lines at g-values of 2.072 and 2.002, which are well in line with expectations based on  $O_2^-$  radicals observed on MgO powder [10.156-158]. In line with theoretical predictions the radicals show significant stability ( $T_{\rm des} \approx 350 \,\rm K$ ) and disappear for thicker MgO films (> 15 ML). A detailed analysis of angle dependent spectra reveals that the  $O_2^-$  radicals are adsorbed on the terraces of the MgO(001) surface aligned with [110] equivalent directions as predicted theoretically (Fig. 10.18b). A comparison of the  $g_{zz}$  component (for an alignment of the g-matrix with the molecular framework see Fig. 10.18c) of the g-matrix ( $g_{zz} = 2.072$ ) with values observed for O<sub>2</sub><sup>-</sup> radicals on terraces of MgO powders ( $g_{zz} = 2.091$ ) [10.157] provides additional physical insight into the interaction between the molecule and the surface as the observed value depends critically on the local electric field experienced by the radical. The reduction of the  $g_{zz}$  component on the film as compared to bulk MgO is associated with an increase of the local electric field, which is due to the polaronic distortion of the MgO lattice in case of the ultrathin film (Fig. 10.18b) as revealed by quantum chemical calculations [10.148].

We have already shown that single Au atoms become charged upon adsorption on very thin MgO(001) films. Hence, it is interesting to explore the consequences of charge transfer on the growth mode of Au particles. Theory predicted that charge transfer onto the gold particles leads to the formation of 2-dimensional structures on ultrathin MgO films in contrast to expectations on bulk MgO, where 3-dimensional particles are expected [10.9, 10, 26]. The reduced stability of the 2dimensional structure with film thickness is due to a decreasing stabilization due to the image charge as well as the increasing cost for the polaronic distortion with increasing film thickness. The latter is caused by a stiffening of the MgO lattice due to the long-range nature of the Coulomb interaction. A low temperature STM study provided experimental evidence for the predicted crossover in growth mode. For an 8 ML MgO/Ag(001)film 3-dimensional particles are observed after annealing to room temperature, whereas the Au-structures on 3 ML MgO/Ag(001) stay 2-dimensional after the corresponding annealing step (Fig. 10.19) [10.27].

An increase of the contact area between metal and oxide film allows to optimize the charge transfer. For a close-packed Au layer on an ultrathin MgO(001)/Ag(001) an average charge transfer of about



# Part B | 10.3

-0.2|e| per adatom has been calculated [10.159]. As shown for Au chains on alumina/NiAl(110) it is not expected that the charge distribution within Au islands is homogeneous [10.160]. Experimentally, this distribution can be interrogated by so-called conduction maps, which show an enhanced dI/dV contrast around the Fermi level at the island edges indicating a higher density of states at these sites [10.161]. This observation is nicely reproduced by semi-empirical tight-binding DFT calculations, which reveal an increase of charges at the perimeter of the particles [10.161].

A more detailed picture of the electronic structure of the adsorbed Au particles can be obtained by exploring so called quantum well states (QWS), which are derived from the 6 s levels of the Au atoms and hence allow for an analysis in a 2-dimensional electron gas model [10.162]. Figure 10.20a,b shows three STM images providing information on topography as well as electronic structure of occupied as well as unoccupied states of a small Au cluster with about 10 Å diameter grown on a 2 ML MgO/Ag(001) film [10.159]. The image taken around the Fermi energy reveals mainly the



**Fig. 10.20** (a) STM images of a symmetric Au cluster on 2 ML MgO/Ag(001) taken at the given sample bias. (b) dI/dV spectra of top (*dark brown*) and left part (*light brown*) of the Au cluster in panel (a). (c) Calculated images of the HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) as well as structure model of an Au<sub>18</sub> cluster on MgO/Ag(001). Reprinted with permission from [10.161]. Copyright (2009) by the American Physical Society

cluster morphology as no states are available in the energy range probed by the STM experiment. At higher bias the appearance of the cluster changes to flowerlike protrusions. The bias-dependent contrast is clear evidence for tunneling governed by electronic and not topographic properties of the island. Both observed QWS probed by STM resemble the eigenstates of a free-electron gas in a 2-dimensional parabolic potential, which can be characterized by an angular momentum quantum number j [10.163]. Both states, observed at -0.4 and +0.8 V, respectively, exhibit four nodal planes (j = 4), which corresponds to G-symmetry. The next two lower lying occupied states, found at -0.8 and -1.2 V, exhibit P-symmetry (not shown). A detailed analysis of the electronic structure of this Au cluster including its charge state was achieved by comparing the experimental results to DFT calculations [10.159]. However, an extensive search of the parameter space is required to determine the number of atoms, the geometric structure as well as the charge state of the cluster. The degree to which theory is able to reproduce the experimental results is nicely shown in Fig. 10.20c assuming a planar Au<sub>18</sub> cluster lacking one corner atom of a Au<sub>19</sub> cluster, the latter being a so-called magic-size. In agreement with the experiment, the highest occupied as well as the lowest unoccupied state are of G-symmetry being located in the 5th level of the harmonic potential, whereas the highest states of the 4th shell of this potential are of P-symmetry in line with the experimental results. Once this has been established, the charge state is readily determined by counting the filled states in the potential. There are 11 doubly occupied orbitals, hence, 22 electrons. The 18 Au atoms contribute 18 electrons, which leads to a 4-fold negatively charged cluster being provided by charge transfer from the support. A Bader analysis of the DFT calculation yields a value of -3.54|e| for the Au<sub>18</sub> cluster. Please note that this amounts to an average transfer of almost 0.2|e| per atom as calculated for closed-packed Au layers on the MgO thin film [10.161].

In this chapter we have discussed charge transfer effects on ultrathin oxide films using MgO as an exploratory example. We have shown how microscopy as well as spectroscopy can be used to provide experimental evidence for charge transfer between the substrate and adsorbed species such as metal atoms or molecular adsorbates with appropriate properties. The tools and concepts used here are, however, not limited to the ultrathin films, but it is possible to transfer some of them to bulk like oxide films if suitable electron donors or acceptors are provided. Such species can be introduced into oxide films by doping, which will be discussed in more detail in following section.

#### 10.3.2 Modifying the Properties of Oxide Materials via Doping

The former paragraphs have illustrated that spontaneous electron transfer through oxide thin films has an enormous impact on the equilibrium shape of metal particles and even enables molecular activation [10.27, 148]. So the question arises, whether the concept of charge-mediated control of the oxide properties is restricted to ultrathin films, or can be extended to thicker layers or even bulk materials, as used in heterogeneous catalysis [10.29, 164]. A possible route might be the insertion of suitable charge sources directly into the oxide material, preferentially into a near-surface region to allow for charge exchange with adsorbates [10.165]. By this means, all advantages of charge control could be maintained for oxide slabs of arbitrary thickness. Although the fundamental concepts of doping were introduced and brought to perfection in the semiconductor technology already decades ago, a direct transfer to oxide materials is challenging due to several structural and electronic peculiarities [10.166]. Oxides are subject to self-doping by native defects and unwanted impurities, the concentration of which is difficult to control experimentally [10.138]. Both lattice defects and impurity ions may adopt different charge states in the oxide matrix [10.167], a variability that leads to pronounced compensation effects and is less common in semiconductors. And finally, the dopants may be electrically inactive in wide-gap oxides, as thermal excitation is insufficient to promote electrons from the defect states to the bulk bands. The excess charges thus

remain trapped at the host ions and are unavailable for charge transfer. However, the following examples demonstrate that doping is a versatile approach to tailor the properties of bulk-like oxides as well.

In general, doping is carried out with impurity ions that adopt either a higher or a lower valence state than the native oxide ions [10.165]. Whereas high-valence dopants may serve as charge donors and provide extra electrons, low-valent dopants have acceptor character and may accommodate electrons from suitable adsorbates. In rare cases, charge-preserving doping is realized where geometric and strain effects take the role of the charge transfer [10.168]. Based on the above considerations, we expect that charge donors inserted in an oxide lattice may resume the role of the metal support in the case of ultrathin oxide films. This assumption has first been verified in studies of the growth morphology of gold on crystalline CaO(100) doped with trace amounts of Mo (Fig. 10.21) [10.47]. On the doped oxide, gold was found to spread out into extended monolayer islands, while the conventional 3-D growth prevailed on the nondoped material. Evidently, the donor character of the Mo ions is responsible for the 2-D growth morphology, while the metal-oxide adhesion on pristine CaO(100) is negligible.

According to DFT calculations, Mo dopants in CaO mainly occupy Ca substitutional sites and adopt the typical 2+ charge state of the rock salt lattice. In the 2+ configuration, four Mo 4d electrons are localized in the dopant, three of them occupying  $(t_{2g}-\alpha)$  crystal field states and one sitting in a  $(t_{2g}-\beta)$  level close to the conduction band onset (Fig. 10.21c) [10.169]. Especially, the latter is in an energetically unfavorable position and thus susceptible to be transferred into an acceptor state with lower energy. Such states are provided by the Au ad-atoms that exhibit a half-filled Au 6s affinity level, being ready to take the topmost Mo4d electron. The result is an Au<sup>-</sup> anion that, as discussed before, experiences reinforced bonding to the CaO surface [10.25]. DFT calculations find an increase of the binding energy from  $\approx 1.5$  to  $\approx 3.5$  eV upon doping, whereby the electrically-active Mo ion may be located up to ten layers below the CaO surface [10.47]. Moreover, not only  $Mo^{2+}$  ions are susceptible to electron transfer into gold, but also Mo<sup>3+</sup> and Mo<sup>4+</sup> are active donors as their topmost occupied d states are still higher in energy than the Au 6s affinity level [10.169]. Mo impurities in the CaO lattice are therefore robust electron donors, and as such directly responsible for the 2-D growth of gold found experimentally [10.47].

The presence of suitable dopants is, however, not the only requirement for a stable donor characteristic and also the interplay between dopants and the host oxide governs the redox activity, as shown for Cr-



**Fig. 10.21a–c** STM images of 0.7 ML Au deposited onto (a) pristine and (b) doped CaO films  $(4.5 \text{ V}, 50 \times 50 \text{ mm}^2)$ . The *insets* display close-up images of two characteristic particles  $(-5.0 \text{ V}, 10 \times 10 \text{ mm}^2)$ . (c) PBE (Perdew–Burke-Ernzerhof (DFT functional)) projected state-density calculated for nondoped (*top*) and doped (*bottom*) CaO films in presence of an Au adatom. Reprinted with permission from [10.47]

doped MgO films next [10.170]. Although chromium has a similar electronic structure as Mo, i.e., the same number of d electrons, it is unable to influence the Au growth on MgO supports (Fig. 10.22). Even at high Cr concentration, gold adopts 3-D shapes and hardly any 2-D islands are found on the surface [10.44]. The reason is the low energy position of the Cr  $t_{2g}$  levels in the MgO band-gap, reflecting the large stabilization effect of the MgO crystal field on the Cr electrons. Note that the crystal field in MgO is much stronger than in CaO given the larger lattice parameter of the latter [10.171]. In addition, the Cr ionization energies are higher than those for Mo, and formation of Cr<sup>4+</sup> and Cr<sup>5+</sup> ions is energetically costive. As a result, Cr is able to donate only a single electron to gold, which compares to three in the case of Mo ions in CaO [10.169, 170]. More critically, not even this electron may reach the ad-metal, but is likely captured by parasitic electron traps in the oxides, such as cationic defects or grain boundaries. Cation vacancies or V-centers are the preferred compensating defects for high-valance dopants, as they are able to neutralize the extra charges released by the impurity ions (Fig. 10.22e) [10.166]. According to DFT calculations, the formation energy of a V-center decreases from 8 eV in bare CaO or MgO to 1.0-1.5 eV in the presence of high-valence dopants [10.44]. Accordingly, an effective compensation mechanism becomes available that fully annihilates the donor character of the Cr ions. Because Mo impurities in CaO are able to release more electrons, full charge compensation is impossible and the impact of the donors prevails in that case.

Low-valence dopants generate hole-states in the electronic structure of rocksalt oxides and are able to trap excess electrons as well [10.172, 173]. Their response is therefore similar to the one of compensating lattice defects, as shown in a codoping experiment on CaO using both, Mo donors and Li acceptors [10.46]. At low Li concentration with respect to Mo, most of the Au particles still adopt 2-D shapes, indicating that the charge transfer into the gold is maintained. With increasing Li doping level, more and more charges get trapped in the Li-induced defects until the charge flow into the ad-gold breaks down completely and the Au particles turn 3-D. In fact, monovalent Li<sup>+</sup> substituting a  $Ca^{2+}$  ion produces a deep hole in the O 2p states of adjacent oxygen that effectively traps all available free carriers and neutralizes the Mo donors. Let's note that Li doping alone did not result in any observable change in the Au growth characteristic on the CaO surface. This finding suggests an effective intrinsic compensation mechanism to be active also in the case of lowvalence dopants [10.174]. Hereby, oxygen vacancies play the role of the compensating defect, as they are able to release electrons according to

$${\rm F}^0 \to {\rm F}^+ + {\rm e}^- \to {\rm F}^{2+} + 2\,{\rm e}^-$$

which then fill up the hole states produced by the Li ions. Hole-doping of oxides, as a means to tailor the properties of metal ad-particles, is therefore more difficult to realize than electron-doping with donor-type impurities [10.175].

So far, electron-transfer processes induced by dopants in the oxide lattice have been shown to modify the growth behavior of ad-metals on oxide surfaces. However, charge exchange is also a promising route for molecular activation, as demonstrated before for oxy-



Fig. 10.22a–e STM images of (a) bare and (b) Mo-doped CaO(100) films of 60 ML thickness after dosing 0.5 ML of Au  $(60 \times 50 \text{ nm}^2, V_S = 6.0 \text{ V})$ . The 2-D Au islands appear as depressions on the insulting oxide, because electron transport through the gold is inhibited at high positive bias. Similar measurements on (c) bare and (d) Cr-doped MgO(100) films of 20 ML thickness. The particle shape is not affected by the dopants in this case. (e) Ball models visualizing charge-transfer processes between the doped oxide and the ad-metal and their effect on the particle shape

gen exposed to thin MgO/Mo films [10.148]. In the following section, we will show that a similar scheme holds for bulk-like oxides, in which high-valence dopants have been inserted as intrinsic charge source.

Not unexpectedly, stoichiometric CaO(100) as a chemically inert, wide gap insulator shows little activity toward adsorption and dissociation of oxygen (Fig. 10.23a) [10.176]. Neither at room nor low temperature (20 K) is the oxide able to bind oxygen, apart from some trace amounts attached to low-coordinated edge and corner sites. This situation changes considerably for a material doped with Mo ions [10.43]. The STM images now reveal a high concentration of depressions on the CaO surface after oxygen exposure, both at 20 and 300 K (Fig. 10.23b). In fact, two oxygen species are distinguished on the surface. The first one shows up as 0.6 Å deep and 10 Å wide depression and is assigned to an oxygen molecule (Fig. 10.23c). Exposing it to electrons from the tip, it can be converted into a pair of shallow dents surrounded by a bright halo. Apparently, the molecule gets dissociated into its atomic

constituents via electron injection [10.177]. Whereas a mean O–O separation of 10-15 Å is observed directly after dissociation, the distance increases over time, indicating the repulsive character of the O–O interaction on the surface (Fig. 10.23c).

The ability of the CaO(100) surface to adsorb oxygen is apparently triggered by the presence of high valence Mo ions in the lattice. The underlying interaction mechanism relies again on an electron transfer between the high-lying Mo4d states and the LUMO of the oxygen molecule, as revealed by DFT calculations performed at the B3LYP (Becke, three-parameter, Lee–Yang–Parr (DFT functional)) +D level [10.43]. On nondoped CaO(100), the oxygen physisorbs with  $\approx$ 0.13 eV to a Ca-Ca bridge position. On doped CaO, an  $O_2^-$  species develops due to charge transfer from the Mo dopants, which strongly interacts with a surface  $Ca^{2+}$ ion. The calculated binding energy amounts to 0.87 eV if the associated donor is a Mo<sup>3+</sup> ion located in the third subsurface plane. Even larger adsorption energies are found for Mo<sup>2+</sup> species serving as donor, as well as



Fig. 10.23 (a,b) STM images of bare and Mo-doped CaO after dosing 5 Langmuir  $O_2$  at 20 K (40 × 40 nm<sup>2</sup>). (c) Biasdependent contrast and height profile of oxygen molecules (deep minima) and atoms (faint double dents). Note the dissociation of an  $O_2$  in the *lower left part* of the image during scanning. (d) Appearance of charging rings, characteristic for subsurface Mo dopants, after desorbing two  $O_2$  molecules from the surface (17 × 17 nm<sup>2</sup>). Reprinted with permission from [10.43]

for dopant positions closer to the surface [10.43]. Further evidence for the formation of  $O_2^-$  species comes from the bond elongation (121-133 pm) and the reduced stretching frequency  $(1537-1200 \text{ cm}^{-1})$  of the oxygen molecule after charge transfer. In addition, a decreasing total spin of the system has been calculated, evolving from 5/2 (3/2 for Mo<sup>3+</sup> plus 2/2 for neutral  $O_2$ ) to 3/2 (2/2 for Mo<sup>4+</sup> plus 1/2 for the  $O_2$ ) due to the electron exchange. The superoxo species formed on the doped CaO surface exhibits, finally, a two times lower barrier for dissociation, if compared with a neutral  $O_2$  on pristine CaO. This theoretical finding is in good agreement with the observation that oxygen adspecies can be effectively dissociated via electron injection from the tip. The DFT calculations therefore clearly corroborate the idea that electron transfer from Mo dopants is responsible for the adsorption, activation and finally dissociation of O2 molecules on the CaO surface [10.43].

Further experimental evidence supports the above mechanism. If single oxygen molecules are removed from the surface by means of a controlled bias pulse given to the STM tip, a Mo donor shows up via a characteristic ring structure on the CaO surface, arising from a temporal change of the Mo charge state as the tip scans this oxide region (Fig. 10.24d). The spatial correlation between the impurity position in the oxide and the preferred  $O_2$  adsorption site underlines that the dopant indeed mediates the binding of oxygen. Interestingly, the active dopant never occupies a position directly in the CaO top layer, but sits in subsurface planes as deduced from the diameter of characteristic charging rings emerging in the STM images [10.178]. The charge transfer to adsorbates hereby occurs via electron tunneling over distances as large as 1 nm. A last experimental hint for O<sub>2</sub><sup>-</sup> formation on doped CaO films comes from the evaluation of the vacuum states above the oxide surface (Fig. 10.24). As mentioned already in Sect. 10.2.1, the vacuum states are a sensitive probe of the local surface potential [10.86] and up-shift in energy if negatively charged species accumulate at the surface but downshift on surfaces holding a positive netcharge. This provides a direct probe of the direction of charge transfer in the CaO/Mo(001) system. An oxide region densely covered with O<sub>2</sub><sup>-</sup> species exhibits a series of vacuum states, the lowest of which being located

![](_page_26_Figure_1.jpeg)

Fig. 10.24 (a,b) Conductance images of CaO/Mo(001) before and after desorbing  $O_2$  molecules from the central region with a tip voltage pulse (40 × 40 nm<sup>2</sup>). The bias voltage for imaging has been tuned to the first vacuum state of the oxygen-covered surface (4.0 eV), which consequently appears with bright contrast. After oxygen removal, the local surface potential, and hence the vacuum states, downshift and the affected surface region shows lower conductance and appears dark. (c) STM conductance spectra showing the energy shift of CaO vacuum states after  $O_2$  desorption from the surface. Reprinted with permission from [10.43]

at 4.2 V above the Fermi level (Fig. 10.24c) [10.43]. After desorbing the molecules with a tip pulse, the vacuum states experience a clear downshift, reflecting the decreasing electron density after removing the negatively charged superoxo species. The excess electrons released during desorption return to their Mo host-ions located in subsurface CaO planes, where they do not perturb the surface potential anymore. The effect of a decreasing surface potential after oxygen desorption can best be visualized in work function maps, plotting the contribution of selected vacuum states to the electron transport between tip and sample (Fig. 10.24a,b). Whereas the overall electron transmissibility is high on the oxygen covered surface, with the exception of certain CaO line defects, a localized patch of low contrast emerges after removal of the  $O_2^-$  species from this region. The measurement reflects the local drop of the surface potential after oxygen desorption, which suddenly makes the lowest vacuum state unavailable for electron transport and explains the low contrast in this region. Also this data cannot be explained without taking the effect of charge transfer between the doped oxide and the O2 molecules into account.

In summary, doped bulk oxides display in many respects similar adsorption properties as ultrathin oxide films [10.179]. In both systems, excess electrons are transferred into the ad-species and open up specific charge-mediated interaction schemes. Whereas for ultrathin films, the extra electrons are provided by the metal substrate below the film, doped oxides contain intrinsic charge sources in the form of aliovalent impurity ions. As shown here, high-valence dopants in the CaO lattice are able to alter the equilibrium shape of metal particles from 3-D to 2-D, which is expected to change the reactivity pattern of the metal–oxide system as well. Moreover, the charge transfer opens a suitable pathway to activate small molecules, such as oxygen or carbon dioxide, even on smooth, defect-free surfaces of a nonreducible, but doped oxide. Whereas thin oxide films on metal single crystals are of large academic interest, as they provide easy access to the properties of oxide materials via conventional surface science methods, doped oxides are of direct, practical relevance for heterogeneous catalysis.

#### 10.3.3 Metal Deposits on Silica Films

In order to make use of the silica film system in the context of heterogeneous catalysts and to further characterize its chemical and physical properties, the adsorption behavior of

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"Au and Pd over bilayer SiO<sub>2</sub>/Ru has been investigated by using scanning-probe microscopy, XPS, and density functional theory (DFT) [10.180]. Low temperature ( $\approx 5$  K) AFM and STM measurements reveal the presence of small adsorption features after exposing the samples to small doses of either metal (Fig. 10.25a,b). In the case of

![](_page_27_Figure_1.jpeg)

Fig. 10.25a-c STM images showing Pd and Au adsorption over silica. (a) Pd on  $SiO_2$ ; (b) Au on  $SiO_2$ . Crystalline regions are colored purple and amorphous regions are colored brown. Note: The nonregular dimmer features throughout the crystalline portions of both samples likely result from native SiO<sub>2</sub>/Ru species, as they are present both before and after metal adsorption. All images:  $15 \text{ nm} \times 15 \text{ nm}$ ,  $V_{\text{S}} = 2 \text{ V}$ ,  $I_{\rm T} = 100 \, \text{pA.}$  (c) Penetration profiles for Pd and Au through rings of different size. Energies are computed with respect to the metal atom in the gas phase. In the left panels the *n* membered  $SiO_2$  rings (MR) are reported (n = 4-8; brown and gray represent Si and O atoms, respectively). Reprinted (adapted) with permission from [10.180]. Copyright (2014) American Chemical

Pd, we note a homogeneous distribution of adsorbates across the entire surface, marked by circles and elemental symbols (Fig. 10.25a), which consists of both amorphous and crystalline phases. Au, however, adsorbs only over amorphous areas and domain boundaries, which possess larger pores than can be found in the ordered portions of the film (Fig. 10.25b). DFT calculations reveal that this difference is rooted in the pore-size-dependent barriers for diffusion of the two metals into the film, where they can then bind stably at the Ru interface (Fig. 10.25c). Auger parameter analysis of the Pd 3d and Au 4f core-levels from atoms binding in this manner show upward orbital-energy shifts, which, according to the results of theoretical calculations, originate from effects similar to those causing surface core-level-shifts for such metals [10.181]. Further analysis of the computational results shows that such atoms donate electron density to the Ru support, which is consistent with XPS results that show band-bending effects related to decreases in the work function of the sample after adsorbing either metal. Additional features in the XPS studies suggest that a secondary binding mechanism, mediated by cluster formation over the SiO<sub>2</sub> film, becomes increasingly favorable as temperature and loading increase."

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For the crystalline  $SiO_2$  film on Mo(112), a similar size-dependent adsorption behavior has been observed. Whereas Pd and Ag atoms were found to penetrate the six-membered -Si-O- rings with little barrier, Au atoms can pass the silica over-layer along do-

#### 10.4 Chemical Reactivity of Oxide Surfaces

Chemical reactions at oxide surfaces play a pivotal role in a variety of technological processes in particular in heterogeneous catalysis. Therefore, it is of great interest to understand these processes at the atomic level. Tremendous efforts have been made for powdered materials to get to this point, but the complexity of these systems usually hampers an atomistic characterization. In this section we will exemplify the level of understanding that can be achieved by discussing first the interaction of water with oxide surfaces as well as the impact of hydroxylation on the growth of metal nanoparticles using the systems introduced above. Subsequently, we will focus on chemical transformations of gas phase molecules on oxide surfaces using vanadium oxide as an exploratory example and will finally show results on CO oxidation on an thin FeO(111) film grown on Pt(111) at elevated pressures and molecular beam studies on alkene hydrogenation as well as the  $H_2/D_2$ exchange reaction using a model catalyst consisting of oxide supported metal nanoparticles.

#### 10.4.1 Interaction of Gas-Phase Water with Well-Defined Oxide Surfaces

The interaction of water with oxide surfaces is of major interest in surface science because of the strong impact of hydroxyl groups on the surface properties, in particular, the reactivity of solid surfaces, which is important in diverse fields such as biology, materials science, environmental science, geochemistry, and heterogeneous catalysis. Depending on the chemical potential of water (and oxygen) and the chemical properties of the oxide surface, the adsorption state of water is either molecular or dissociated, or a combination of the two.

main boundaries only, which contain larger, i.e., eightmembered rings [10.182]. However, it is not the size of the atoms that governs the penetration behavior, but their electronic structure. Both, Pd and Ag atoms deplete their spatially expanded 5s orbital before passing the film, while the highly electronegative Au cannot strip off its 6s-electron and is thus unable to penetrate the regular SiO<sub>2</sub>. Inserting metal atoms at the interface between ordered silica films and the Mo support opens a number of other fascinating functionalities. Addition of interfacial Li, for example, gives rise to a dramatic decrease of the work function of the thin film system, controlled by the highly electropositive character of the Li-ions [10.183]. Iron deposition, on the other hand, leads to the formation of single-ion magnetic units at the metal-oxide interface [10.184].

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"In this section, we review some of the results obtained with the thin oxide films introduced in Sect. 10.2 with regard to water interaction, showing how a combination of different methods allows to gain atomistic insight into the energetics of adsorption processes as well as the nature of the surface species.

#### Water on Alkaline Earth Oxide and Silica Surfaces: Monolayer Structures and Hydroxylation

A comparison of water adsorption on the (100) surfaces of the alkaline earth oxides is interesting because they all have the same structure (fcc, rocksalt), but different lattice constants and basicity, which is expected to strongly influence the water adsorption (molecular or dissociative) and the ability to form long-range ordered 2-dimensional structures. While monolayer water adsorption on MgO has extensively been studied in the past both experimentally and theoretically and is now well-understood, details about the higher alkaline earth oxides such as CaO and SrO have only recently become available. It is well established that a single water molecule adsorbs molecularly on the MgO(100) surface, but may dissociate, even under UHV conditions, on defects such as low-coordinated cation-anion pairs on step edges. By contrast, single molecule adsorption is dissociative on CaO and SrO and involves considerably higher adsorption energies, as shown in Fig. 10.26a, which displays the computed  $E_{ads}$  for water on the various oxides [10.185]. The dissociated monomer consists of a dynamic ion pair with the hydroxyl group (free OD, OD<sub>f</sub>) adsorbed in bridge position between two cations and the proton transferred to a nearby oxygen ion (surface OD, O<sub>s</sub>D, Fig. 10.26c) [10.186]. An interesting trend is seen for increasing water coverage, i.e., for increasing the number of water molecules per  $(3 \times 4)$  unit cell used in the calculations: While the adsorption energy increases with increasing coverage for MgO and 2-dimensional monolayer structures are found to be the most stable water adsorption states, the calculated adsorption energy for water on CaO(001), although very similar in the entire coverage range, is highest for 1-dimensional structures. For SrO, isolated and dissociated monomer and dimer species are expected to be more stable than the oligomer species. Experimentally, evidence for the 2-dimensional ordered arrangement of the water monolayer on MgO has been provided by diffraction and scattering methods more than 20 years ago [10.187, 188]. More recently, the stability of 1-dimensional water structures was proven by STM upon water adsorption on thick CaO(001) films at room temperature (Fig. 10.26b) [10.185, 189], and the confirmation of the dynamic ion pair nature of a single, dissociated water molecule, as well as the stability of dimer species, on SrO has been obtained by STM on SrO-terminated Sr<sub>3</sub>Ru<sub>2</sub>O<sub>7</sub> [10.190].

Generally, diffraction methods and STM do not allow the positions of the individual water species and their chemical nature (molecular or dissociated) within the 1- and 2-dimensional water structures found on MgO(001) and CaO(001) to be determined, and one has to resort to high-level computations and spectroscopic methods to learn more about the molecular-scale details of these structures. Whereas electron spectroscopies can provide information about the presence of dissociated and molecular water, which, for example, has provided first experimental proof for the existence of mixed molecular/dissociated water molecules in the water monolayer on MgO(001) [10.192], comparison of experimentally measured and computationally obtained frequencies of water and hydroxyl vibrations is considered to provide additional information about the structural details.

The latter approach has been used to identify and confirm the structural models of the 2-dimensional water monolayer on MgO(001) [10.191], and of the 1-dimensional chain structures found by STM on CaO(001) [10.185, 189]. Figure 10.26d shows the experimental IRAS (infrared reflection absorption spectroscopy) spectra (top panel) for the water monolayer prepared on MgO (left panel) at low temperature (160 K), and for the water chain structures prepared on CaO(001) at room temperature (right panel), and the corresponding calculated anharmonic vibrational spectra (lower panel). (Note that the experiments and calculations were performed with D<sub>2</sub>O instead of H<sub>2</sub>O). The experimental spectra are qualitatively similar and exhibit reasonably narrow bands in the range 2600-2750 cm<sup>-1</sup> and broad absorption between 2000 and 2500 cm<sup>-1</sup>. The individual spectral contributions can be assigned based on the good agreement between the experimental spectra and the calculated spectra of the most stable structures shown in Fig. 10.26. For both, the MgO(001) and CaO(001) surface, the ordered water structures are comprised of dissociatively and molecularly adsorbed water. In the case of MgO, two ordered structures with different water coverage, the high coverage  $c(4 \times 2)$  and the low-coverage  $pg(3 \times 2)$ structure, coexist at 160 K and can be distinguished based on the different frequencies of the OsD groups [10.191]. Note that, due to the metal surface selection rule, the molecular water species, which are oriented almost parallel to the surface in both structures, give rise to only weak absorption signals. In fact, they do not contribute to the IR spectrum of the  $pg(3 \times 2)$  structure. In the case of the  $c(4 \times 2)$  structure, the molecular water species stabilize the protruding OH<sub>f</sub> group, and combinations of their symmetric and anti-symmetric stretch vibrations lead to signal contributions in the 2100-2400 cm<sup>-1</sup> spectral range, which are detected in the experiment as a broad featureless absorption. Molecular water species in the 1-dimensional chain structure on CaO(001) are also oriented parallel to the surface and contribute only little to the IR signal on the thin film sample. The more defined signals for water on CaO(001) originate from OH<sub>f</sub> (at highest wavenumber) and OsD groups from dissociated water. Note that the O<sub>s</sub>D groups in the 1-dimensional chain structure on CaO(001) are spectrally much more separated than in the 2-dimensional structures on MgO because the strength of hydrogen bonding between O<sub>s</sub>D groups and OD<sub>f</sub> groups is markedly different in the tetramer unit and in the linker unit [10.185].

The combined experimental and computational analysis of water adsorption on the alkaline earth oxides has not only contributed to a better understanding of the molecular details of wa-

![](_page_30_Figure_1.jpeg)

#### Fig. 10.26

adsorption energy per water molecule on CaO(001), MgO(001), and SrO(001) for increasing water coverage (1w, etc.: 1 water molecule per  $(3 \times 4)$  unit cell; 1-D, etc.: 1-dimensional water/hydroxyl structures). (b) RT-STM image  $(30 \times 25 \text{ nm}^2)$  of 1-dimensional water chains formed on CaO(001). (c) Most stable structures of the dissociated water monomer on CaO(001), the 1-D chain structure on CaO(001), and the two most stable ordered 2-D water phases  $(pg(3 \times 2))$ and  $c(4 \times 2))$  on MgO(001). (d) Experimental (top) and computed (bottom) IR (infrared) spectra of the 2-D (D<sub>2</sub>O) structures on MgO(001) (left) and the 1-D  $(D_2O)$ chain structure on CaO(001) (right). After [10.185, 189, 191]

ter structures, but additionally allows conclusions about the evolution of different structures on the surfaces to be drawn. Dissociation of a single water molecule is favored and involves larger adsorption energies when going from MgO to SrO. This can be explained by the increasing lattice constant and substrate flexibility when descending the AEO series [10.193]. Additionally, the subtle balance between intermolecular and moleculesurface interactions determines also the stability of higher coverage structures: Two-dimensional ordered structures are stabilized on MgO(001) because of the weak interaction between water and the MgO surface and the favorable dimension of the MgO lattice parameter, which allows a strong hydrogen bonding network between adsorbed water and hydroxyl species to be established. The CaO lattice is slightly too large to enable the formation of a hydrogen-bonded network, and the water structures therefore collapse into a 1-D configuration at low coverage. Similar 1-D assemblies become stable also on MgO(001) when its lattice parameter is artificially increased to reduce the effect of intermolecular coupling. In contrast on SrO(001), the water residuals are always too far away to form uniaxial or 2-dimensional hydrogenbonded arrangements [10.185].

The results presented for the alkaline earth oxides demonstrate that not only the acid-base properties of the oxide surface, but also the lattice parameter and hence, the ability to form hydrogenbonds between neighboring hydroxyl groups, has a major impact on the adsorbed water structures.

The examples discussed so far refer to water adsorption on bulk-like thin films (i.e., films of reasonable thickness and structurally similar as the corresponding bulk oxides) at UHV conditions, where no structural modifications of the oxide lattice take place during adsorption. For complete hydroxylation of the oxide surfaces, which is expected to occur when environmentally more realistic water partial pressure conditions (mbar range) or higher water coverages are approached, reactions between water and the oxide surfaces have to be considered as well. For the more ionic oxides in particular, this may involve hydrolysis of cation-anion bonds and strong structural modifications. The hydroxylation of MgO and CaO single crystal surfaces and the partial transformation into the corresponding hydroxide as a function of relative humidity have been studied by ambient pressure XPS. Those studies revealed that the CaO(001) surface gets fully hydroxylated even under UHV conditions and transforms into the hydroxide, involving hydroxylation of the subsurface regions, at elevated water partial pressure [10.194]. On the other hand, a certain threshold water pressure in the sub-mbar range has to be applied to achieve sufficient surface hydroxylation of MgO(001) [10.195]. Studies on the corresponding thin film surfaces confirmed these results. Figure 10.27a compares STM images of the surface of a clean CaO(001) film (top) and after a saturation dose of water under UHV conditions at room temperature (bottom) [10.185, 189]. Clearly, water adsorption leads to strong structural modification of the surface, which is due to complete surface hydroxylation and partial solvation of Ca<sup>2+</sup> ions. The latter can in part be explained by the sufficiently large structural flexibility of the CaO lattice, which allows easy rupture of cation-anion bonds.

By contrast, hydroxylation of thick, bulk-like MgO(001) films at room temperature and in UHV conditions is limited to defect sites, and in order to obtain complete hydroxylation a threshold water partial pressure of about 0.01 mbar has to be applied (Fig. 10.27b) [10.196]. Titration of  $Mg^{2+}$ sites with CO has shown that the number of lowcoordinated Mg2+ sites gets strongly enhanced upon hydroxylation, suggesting the occurrence of similar structural modifications as in the case of CaO(001). Interestingly, the threshold pressure for hydroxylation decreases by 3 orders of magnitude as the film thickness is reduced from 12 to 2 ML (Fig. 10.27b) [10.196]. This effect is not related to an increased abundance of defects on the ultrathin film, but can be explained by a decreased energetic barrier for the rupture of  $Mg^{2+}-O^{2-}$  bonds, which is related to the greater structural flexibility of the MgO lattice in the ultrathin regime [10.197].

Polar oxide surfaces are intrinsically reactive towards water because surface hydroxyls provide compensating charges necessary to remove polarity. Similarly, in polar oxide films grown on metal substrates, while the compensating charge density at the metal-oxide interface is readily provided by the metal, the free film surface needs to be compensated by conventional mechanisms, e.g., surface hydroxylation. Conversely, the thinnest oxide films (monolayers) are intrinsically nonpolar, thus reducing their activity towards water. In fact, the FeO(111) monolayer film is stable in pure water vapor environment, as shown by the O1s XP spectrum obtained after exposure to 1 mbar water vapor, which exhibits only one component attributable to the lattice oxygen

![](_page_32_Figure_1.jpeg)

Fig. 10.27 (a) STM images  $(30 \times 25 \text{ nm}^2)$  of 10 ML CaO(001)/Mo(001) (*top*) and of the same surface exposed to a saturation dose of water at RT (*bottom*). Reprinted with permission from [10.189], © ACS (2016). (b) H<sub>2</sub>O pressure dependent surface hydroxyl coverage on Ag(001)-supported MgO(001) films of different thickness obtained from fits of the O 1s XP spectra. Reprinted (adapted) with permission from [10.196]. Copyright (2010) American Chemical Society

species, and no further contribution from hydroxyls (Fig. 10.28a) [10.198]. In addition, the structural integrity of the FeO(111) monolayer appears to be maintained upon exposure to air ambient and even liquid water, as shown by the STM images presented in Fig. 10.28c, where the long-range ordered Moiré superlattice characteristic of FeO(111)/Pt(111) is proven to persist in the corresponding environment.

As will be discussed in more detail below (Sect. 10.4.3), exposure of FeO(111) to a highpressure oxygen atmosphere leads to a transformation of the FeO bilayer to a O-Fe-O trilayer [10.35, 37, 39]. Both, the additional oxygen incorporated in the film, which shows up in XPS as a shoulder on the high binding energy side of the main O1s component (Fig. 10.28a), and the similarity of the STM appearance suggest that this transformation occurs also upon exposure of the FeO film to air. In addition, the IRA spectrum of an air-exposed film reveals the presence of hydroxyl species with characteristic vibrations at  $3650 \,\mathrm{cm}^{-1}$ . It can, therefore, be concluded that the trilayer structure is not only highly active in the catalytic oxidation of CO, but also in water dissociation. As a result, an O-Fe-OH trilayer is formed (Fig. 10.28d) and the additional O 1s signal in XPS can be attributed to hydroxyl species [10.198]. XPS quantification reveals a maximum hydroxyl coverage of 0.45 ML. Together with the ordered appearance in STM this suggests that the hydroxylation activity is restricted to the most reactive region within the Moiré unit cell, which, according to DFT calculations, is the Fe-hcp region [10.37]. Note that also the hydroxylated FeO layer is highly active in CO oxidation [10.198].

All UHV-based, well-defined silica models have a common structural motif, which consists of corner-sharing [SiO<sub>4</sub>] tetrahedra arranged in a honeycomb structure (Sect. 10.2.2) [10.202]. The fact that the surfaces are terminated by siloxane bonds renders the regular parts of the films hydrophobic and, thus, unreactive towards water. Indeed, the silica bilayer on Ru(0001) can be exposed to air and pH neutral aqueous solutions without any noticeable accompanying chemical and structural modifications to the film (see also Sect. 10.5.1). Hydroxylation of these model systems occurs only at defect sites, which, on well-prepared films, are scarce [10.203]. Since hydroxyl groups on silica (silanol groups) are of enormous importance for several technological applications, their creation and further utilization on well-defined model systems may help obtain more fundamental insight into specific interfacial reactions where silanols are involved. Hydroxylation of the films could be achieved with the help of electron bombardment of the water (ice) layer [10.199]. This is exemplified by the TPD spectra shown in Fig. 10.28e, which have been obtained after dosing water  $(D_2O)$  at a substrate temperature of 100 K and followed by heating to RT (normal route, black curve), or with an additional electron bombardment prior to heating (electron-assisted route, red curve). The strong

![](_page_33_Figure_1.jpeg)

**Fig. 10.28** (a) O 1s XP spectra, from *top* to *bottom*, of (i) clean FeO(111)/Pt(111), the film exposed to (ii) 1 mbar D<sub>2</sub>O, (iii) air, and (iv) 100 mbar O<sub>2</sub> and 1 mbar H<sub>2</sub>O. (b) IR spectrum of the FeO(111)/Pt(111) film exposed to 100 mbar O<sub>2</sub> and 1 mbar H<sub>2</sub>O. (c) Ambient-STM images  $(60 \times 60 \text{ nm}^2)$  of the FeO(111)/Pt(111) film in air (*top*) and in liquid water (*bottom*). Reprinted with permission from [10.198], © (2011) American Chemical Society. (d) Model of the FeO(111)/Pt(111) film (*left*) and of the Pt–O–Fe–OH film (*right*) formed by exposure to air. (e) TPD (temperature programmed desorption) spectra ( $m/z^+ = 20$  amu) of SiO<sub>x</sub> samples exposed to 5 Langmuir D<sub>2</sub>O at 100 K and then exposed (*e-beam, light brown* trace) or not exposed (*normal, dark brown* trace) to an electron beam (0.05 mA, 200 eV, 60 s). (f) Hydroxylation structures for silica films involving breaking of in-plane (structure Ia, *top*) and vertical (structures Ib and II, *bottom*) siloxane bridges, obtained from DFT calculations. Reprinted (adapted) with permission from [10.199]. Copyright (2011) American Chemical Society

enhancement of water desorption from the electron-bombarded sample in this region is related to a significantly increased abundance of  $D_2O$  and OD's on the silica surface. More specifically, the thermal route leads to the formation of isolated hydroxyl groups at defect sites within the film, which recombine at elevated temperature and desorb as molecular water at 900 K, and some additional hydrogen-bonded physisorbed water, which desorbs at lower temperatures (< 500 K). The small amount of water desorbing from this sample supports the idea of the inert nature of the silica bilayer film surface. By contrast, enhanced hydroxylation of the electron-bombarded sample gives rise to much larger and more clearly defined water desorption peaks with maxima at 450 and 600 K, as well as an additional high temperature desorption feature at  $\approx 1070 \text{ K} [10.199, 204]$ . It is interesting to see that in terms of peak temperatures associated with individual desorption states, there is general agreement with analogous TPD spectra collected from hydroxylated bulk silica samples,

![](_page_34_Figure_1.jpeg)

**Fig. 10.29 (a)** STM topographs ( $50 \text{ nm} \times 50 \text{ nm}$ ) of 0.2 ML of Au deposited on clean (*top*) and hydroxylated MgO(001)/Mo(001) (*bottom*) at RT (*left*) and after annealing at 600 K (*right*) [10.200]. (b) *Top*: TPD spectra tracking the  $m/z^+ = 4$  (D<sub>2</sub>) evolution from hydroxylated MgO (*gray*) and hydroxylated MgO with 0.4 ML Pd (*brown*) deposited at RT. Reprinted (adapted) with permission from [10.200]. Copyright (2011) American Chemical Society. (b) *Bottom*: Temperature-dependent Pd 3d electron binding energy variations relative to Pd(111) due to changes in the initial states of the photoemission process for Pd–MgO (*black*) and Pd–MgO<sub>hydr</sub> (*brown*). Reprinted (adapted) with permission from [10.201]. Copyright (2014) American Chemical Society

which suggests the presence of similar water and hydroxyl species on the hydroxylated silica film. According to the Zhuravlev model [10.205], the desorptions are attributed to the following adsorption states and processes: Chemisorbed molecular water gives rise to desorption at 400 K, whereas the high temperature peaks are assigned to recombinative water desorption originating from vicinal (at 600 K) and isolated hydroxyls (above 800 K). The creation of silanols requires the rupture of siloxane bridges and several possibilities how this could be achieved have been modeled by DFT [10.199]. As shown by the structural models presented in Fig. 10.28f, rupture of an in-plane siloxane bridge results in two silanol groups, which are both engaged as donor groups in hydrogen bonds (structure Ia). On the other hand, breaking the Si-O-Si linkage between the two silicate layers results in one hydrogen-bonded silanol and one terminal silanol species (structure Ib). In addition to these processes, which are basically the same as assumed for bulk silica surfaces, the presence of the metallic substrate underneath the silica film opens the possibility for another mechanism, which involves hydrogen release and Ru oxidation (structure II). According to the computed hydroxylation energies and further experimental observations (D2 desorption observed in TPD and infrared signals of terminal OD groups) [10.199], all three proposed structures are likely to be formed initially during electron bombardment or are created via transformation of one structure into the other during heating to elevated temperature. Further experimental studies into the mechanism of electron-assisted hydroxylation of the silica films support the idea that the primary effect of electron irradiation is not the creation of defects (i.e., rupture of siloxane bridges) in the films, but the formation of reactive water radiolysis products (e.g., hydroxyl radicals) in the ice layer, which diffuse to the silica-ice interface and attack the siloxane bridges [10.204]."

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#### Metal Nucleation on Hydroxylated Mg0 Surfaces

Controlled creation of hydroxylated oxide thin film surfaces allows the influence of the hydroxyl groups on surface processes to be studied. As an example, the effect of hydroxyls on metal nucleation on hydroxylated MgO is presented. A most conspicuous evidence for the influence of hydroxyls on nucleation and sintering of Au on MgO(100) is provided by STM. The images displayed in Fig. 10.29a present the surface morphology for gold deposited at 300 K and after subsequent heating to 600 K on clean MgO(100) and hydroxylated MgO, respectively [10.200]. Two main conclusions can be drawn from these results: (i) the density of nucleation sites is much higher on MgO<sub>hydr</sub>, and (ii) the stability of Au particles towards sintering is greatly enhanced on MgO<sub>hvdr</sub>. This latter point is essential for catalysis because it basically means that the high Au dispersion is maintained at elevated temperature, a result that is corroborated by related CO-TPD studies showing a higher CO adsorption capacity for  $Au/MgO_{hydr}\xspace$  as compared to Au/MgO(100) [10.206]. With the help of additional XPS and IRAS measurements the enhanced Au sinter stability could partly be explained by the stronger adhesion of Au to the hydroxylated surface, which is a result of the chemical modification (oxidation) of interfacial Au because of the interaction with hydroxyls [10.200]. In addition, one has to take into account that the microscopic roughness of MgO increases upon hydroxylation [10.196], which might also contribute to limited diffusion of Au clusters on the surface.

Similar experiments have also been performed with Pd instead of Au, and in this case more details about the chemical interaction between the metal atoms and the surface hydroxyl groups could be obtained [10.201]. The interaction of metal atoms with hydroxyls is expected to follow a redox reaction

$$Me + -OH^- \rightarrow -O_2^- -Me^+ + \frac{1}{2}H_2$$
,

resulting in the simultaneous oxidation of the metal and evolution of H<sub>2</sub>. This could indeed be observed with Pd atoms deposited on MgO<sub>hydr</sub> (hydroxylation was performed with D<sub>2</sub>O) as shown in Fig. 10.29b. The top panel displays D<sub>2</sub>-TPD spectra taken from MgO<sub>hydr</sub> and Pd deposited on MgO<sub>hydr</sub>, which shows that the presence of Pd leads to a strong enhancement of D<sub>2</sub> evolution from MgO<sub>hydr</sub> at elevated temperature (> 350 K). To correlate D<sub>2</sub> evolution with electronic structure changes of Pd, Pd 3d spectra and in particular, a deconvolution of the Pd 3d binding energy shift in initial-state and final-state contributions using Auger parameter analysis was performed. The bottom panel of Fig. 10.29b compares the initial-state binding energy shift relative to the Pd 3d binding energy of bulk Pd (352.1 eV) for Pd on clean MgO(001) (black data points) and Pd on MgO<sub>hydr</sub> (blue data points). The shift from negative to positive  $\Delta$ BE values for Pd-MgO<sub>hydr</sub> at 373 K, which correlates with the onset of D<sub>2</sub> evolution from the Pd-MgO<sub>hydr</sub> sample, indicates that Pd gets oxidized at this temperature. Thus, the interrelation of these processes provides direct evidence of the redox reaction between Pd and hydroxyls, which results in Pd oxidation and hydrogen (deuterium) evolution [10.201].

#### 10.4.2 Methanol Partial Oxidation on V<sub>2</sub>O<sub>3</sub>(0001) and V<sub>2</sub>O<sub>5</sub>(001)

An often studied reaction in model catalysis is the partial oxidation of methanol. This can be readily investigated under low pressure conditions since the educt (methanol) as well as the common precursor (methoxy) are reasonably strongly bound to the surface and do not desorb at low pressure and not too high temperature.  $V_2O_5(001)$  and  $V_2O_3(0001)$  were studied with respect to their catalytic performance using the partial oxidation of methanol as a test reaction [10.132, 207, 208]. It turned out that the vanadyl terminated surfaces are not reactive with respect to this reaction since methanol just binds molecularly to the surface without forming the methoxy intermediate [10.132, 208]. Therefore, the surfaces were reduced prior to methanol exposure by electron irradiation. For small electron doses the electron beam leads to the removal of vanadyl oxygen atoms resulting in isolated or aggregated point defects, see Fig. 10.30a,b. The surface structure after irradiation with a high electron dose was studied with I/V-LEED in the case of V<sub>2</sub>O<sub>3</sub>(0001) [10.209]. An STM image is displayed in the right panel of Fig. 10.30. It could be shown that this surface exposes the SM termination as schematically depicted in Fig. 10.14. The dark areas exhibit the same surface structure as the more elevated areas.

The following will discuss methanol adsorption for the case of a low degree of reduction where isolated vacancies or small groups of them prevail. Figure 10.31 shows STM images of a  $V_2O_3(0001)$  surface before electron irradiation, after electron irradiation and after dosage of methanol onto the reduced surface. The point defects found at the surface of a freshly prepared oxide layer (Fig. 10.31a) are not active for methoxy formation, but the vacancies produced by electron irradiation are [10.132]. Therefore, only part of the surface defects is covered by methoxy groups (seen as bright protrusions) in Fig. 10.31c.

STM data of the type shown in Fig. 10.31 were recorded for two different energies of the reducing electrons (50 and 500 eV) and different electron doses

![](_page_36_Figure_1.jpeg)

**Fig. 10.30a-c** STM images on vanadium oxide layers on Au(111) reduced by electron irradiation. (a) Weakly reduced  $V_2O_5(001)$ ,  $20 \times 20 \text{ nm}^2$ , U = 2 V, I = 0.2 nA. (b) Weakly reduced  $V_2O_3(0001)$ ,  $25 \times 25 \text{ nm}^2$ , U = -1.5 V, I = 0.2 nm. (c) Fully reduced  $V_2O_3(0001)$ ,  $20 \times 20 \text{ nm}^2$ , U = -1 eV, I = 0.2 nA. The electron doses (energies) used for reduction are (a) 3 mC (50 eV), (b) 1.5 mC (50 eV), (c) 80 mC (500 eV)

< 0.8 mC (500 eV) and 1.6 mC (50 eV), respectively. In each series the number of defects before and after electron irradiation and the number of methoxy groups after exposure of the surface to methanol were counted. The methanol layer was prepared by dosing multilayer amounts of methanol at 90 K and the STM images of the methoxy-covered surfaces were recorded after a flash to 400 K in order to desorb the molecularly adsorbed methanol.

Figure 10.32 displays the results of the evaluation. The main outcome is that the number of methoxy groups is approximately twice as large as the number of surface defects which is the consequence of a self-limiting chain reaction at the surface [10.132]. In the initial step, which occurs already when methanol is adsorbed at 90 K all electron induced defects carry one methoxy group

 $n \operatorname{CH}_3\operatorname{OH} + n \operatorname{V} + n \operatorname{VO} \rightarrow n \operatorname{CH}_3\operatorname{OV} + n \operatorname{VOH}$  (10.1)

V denotes a vanadium site produced by electron irradiation, VO is a surface vanadyl group, and *n* is the number of surface vanadyl oxygen vacancies.

If the sample is warmed up water forms at 270 K due to the recombination of hydroxyl groups as shown by TPD [10.132]. This reaction consumes substrate oxygen which is the signature of *Mars–van Krevelen* type reactions [10.210]

$$n \operatorname{VOH} \rightarrow \frac{1}{2}n \operatorname{H}_2\operatorname{O} + \frac{1}{2}n \operatorname{VO} + \frac{1}{2}n \operatorname{V}$$
 (10.2)

This step occurs at a temperature where molecular methanol is still at the surface. Therefore, the surface

![](_page_36_Figure_11.jpeg)

**Fig. 10.31a–c** STM data of freshly prepared (a), reduced (b), and methoxy covered reduced (c)  $V_2O_3(0001)$ . Vanadyl oxygen vacancies were prepared by irradiation with 1.5 mC of 50 eV electrons.  $25 \times 25 \text{ nm}^2$ , U = -1.5 V, I = 0.2 nA. After [10.132]

![](_page_37_Figure_1.jpeg)

with its n/2 V sites can split n/2 methanol molecules into n/2 methoxy groups and n/2 hydroxyl groups

$$\frac{1}{2}n \operatorname{CH}_{3}\operatorname{OH} + \frac{1}{2}n \operatorname{V} + \frac{1}{2}n \operatorname{VO}$$

$$\rightarrow \frac{1}{2}n \operatorname{CH}_{3}\operatorname{OV} + \frac{1}{2}n \operatorname{VOH}$$
(10.3)

The n/2 hydroxyl groups produced in this step can again form water

$$\frac{1}{2}n \text{ VOH} \rightarrow \frac{1}{4}n \text{ H}_2\text{O} + \frac{1}{4}n \text{ VO} + \frac{1}{4}n \text{ V}$$
 (10.4)

With this reaction the cycle goes on. The overall number of methoxy groups produced in this reaction is

$$N_{\text{methoxy}} = n + \frac{1}{2}n + \frac{1}{4}n + \ldots = 2n$$
 (10.5)

This is in full agreement with the data in Fig. 10.32.

Figure 10.33 shows the effect of this self-limiting chain reaction on IRAS spectra. The intensity increase of the methoxy C–O vibration at  $\approx 1040 \text{ cm}^{-1}$  can be attributed to the chain reaction occurring at  $\approx 270 \text{ K}$ where the hydroxyl groups at the surface react to form water: the methoxy coverage doubles and so does (approximately) the intensity of the C–O vibrational band. The band labelled V=<sup>18</sup>O and V=<sup>16</sup>O are due to vibrations of vanadyl groups with <sup>18</sup>O and <sup>16</sup>O. The presence of both isotopes is a result of the preparation history of the V<sub>2</sub>O<sub>3</sub>(0001) sample. Fig. 10.32a,b Density of defects induced by electron irradiation and the number of methoxy groups as a function of the electron dose for two electron energies (a) E =50 eV and (b)  $E = 500 \,\text{eV}$ . The data were obtained from STM images like the ones shown in Fig. 10.27 (CH<sub>3</sub>OH/weakly reduced  $V_2O_3(0001)$ ). The number of surface defects in this figure is the number of surface defects in images recorded after electron irradiation minus the number of defects already present at the surface before exposure to the reducing electron beam. After [10.132]

The case of methanol on  $V_2O_5(001)$  is different from the case of methanol on the case for methanol on  $V_2O_3(0001)$  due to somewhat different activation energies [10.132, 207]. The reaction kinetics of methanol on  $V_2O_5(001)$  has been studied in some detail with TPD [10.208]. Figure 10.34 displays the amount of formaldehyde formed by methanol partial oxidation at the surface of slightly reduced  $V_2O_5(001)$  as a function of the methanol dose. This quantity was estimated from the area of the formaldehyde mass 29 desorption peak in TPD spectra. At elevated temperature the methoxy groups react on the surface, forming formaldehyde and therefore the mass 29 peak area is a good measure for the methoxy coverage. The red line in Fig. 10.34 shows the best fit to the data assuming a sticking coefficient proportional to the number of unoccupied adsorption sites. It is clear that this simple model is not correct which means that the reality must be more complex.

Therefore a model considering water formation from hydroxyl groups and methanol formation from methoxy and hydroxyl groups was formulated, i.e., the following two reaction step were incorporated

$$VOH + VOH \rightarrow VO + V + H_2O$$
(water formation) (10.6)

$$VOH + CH_3OV \rightarrow VO + V + CH_3OH$$
 (10.7)

(methanol formation)

![](_page_38_Figure_1.jpeg)

![](_page_38_Figure_2.jpeg)

Fig. 10.33 IRAS spectra of methanol-dosed moderately reduced  $V_2O_3(0001)$  after annealing at 240 and 270 K, respectively. Methanol was dosed at 90 K and the surface was reduced with an electron dose of 8 mC. After [10.132]

Fig. 10.34 TPD formaldehyde peak area (solid black squares) as a function of methanol dose for methanol on weakly reduced V<sub>2</sub>O<sub>5</sub>(001) in comparison with surface methoxy coverages calculated according to two different models (solid red and dashed blue line, see text). The sample was reduced by irradiation with electrons with a kinetic energy of 50 eV, dose: 1 mC. Dosing was performed at room temperature to prevent the formation of a molecularly adsorbed methanol layer. Reproduced from [10.208] with permission of The Royal Society of Chemistry

Herewith the following differential equation system was set up for the time-derivative of the methoxy coverage  $\theta_{\text{M}}$  and the hydroxyl coverage  $\theta_{\text{OH}}$  [10.208]

$$N_{\text{tot}} \frac{d\theta_{\text{M}}}{dt} = S(\theta) \Phi_{\text{M}} - N_{\text{tot}} \theta_{\text{M}} \theta_{\text{OH}} \nu \exp\left(-\frac{E_1}{kT}\right)$$
(10.8)  
$$N_{\text{tot}} \frac{d\theta_{\text{OH}}}{dt} = S(\theta) \Phi_{\text{M}} - 2N_{\text{tot}} \theta_{\text{OH}}^2 \nu \exp\left(-\frac{E_2}{kT}\right)$$
$$-N_{\text{tot}} \theta_{\text{M}} \theta_{\text{OH}} \nu \exp\left(-\frac{E_1}{kT}\right)$$
(10.9)

 $S(\theta)$  is a coverage-dependent sticking coefficient, t is the time,  $N_{\text{tot}}$  is the number of vanadyl lattice

sites  $(4.8 \times 10^{18} \text{ m}^{-2})$ ,  $\nu$  is the attempt frequency (set to  $10^{13} \text{ s}^{-1}$ ),  $E_1$  and  $E_2$  are the energy barriers for methoxy–OH recombination and OH–OH combination, respectively,  $\theta_M$  is the flux of methanol molecules per unit area and time, k is Boltzmann's constant and T is the adsorption temperature (T = 298 K). It is assumed that there are no further reaction paths and that diffusion can be neglected which is reasonable if it is much quicker than the water and methanol formation reactions. The sticking coefficient  $S(\theta)$  is assumed to be coverage-dependent

$$S(\theta) = \frac{N_0 - N_{\rm M}}{N_{\rm tot}} \tag{10.10}$$

with  $N_0$  and  $N_M$  being the number of possible adsorption sites per unit area and the number of methoxy groups per unit area, respectively ( $N_M = \theta_M N_{tot}$ ). Methanol molecules that hit the surface at an unoccupied defect site do stick, while molecules that hit a nonreduced or occupied surface site do not. We note that the calculated water and methanol formation rates are three orders of magnitude smaller than the rate at which methanol molecules impinge onto the surface. Therefore the reactive defect sites are nearly fully covered and details of the sticking coefficient equation do not play a relevant role.

The set of differential equations was solved numerically with  $E_1$  and  $E_2$  as parameters to fit the experimental data in Fig. 10.34.  $N_0$  was set to 7.5% which is approximately the density of surface oxygen vacancies after exposing the surface to 1 mC of electrons with a kinetic energy of 50 eV. The best fit was obtained for  $E_1 = E_2 = 0.85 \text{ eV}$  (blue curve in Fig. 10.34). The blue curve reproduces the experimental data quite well and the activation energies for water and methanol formation are indeed identical within the error range of the fit. Somewhat similar activation energies ( $E_1 = E_2 = 0.75 \text{ eV}$ ) could be obtained from a fit of TPD data [10.208].

These studies highlight the role of hydroxyl groups in the methanol partial oxidation reaction. Hydroxyl groups are not just spectators in this reaction (with the side effect that they reduce the substrate when they react to form water), they can affect the kinetics and therefore the reaction rate. They may also affect the selectivity as observed for  $V_2O_3(0001)$  [10.132] (not discussed here).

#### 10.4.3 Strong Metal Support Interaction Effects on Reactivity: Fe0/Pt in CO Oxidation

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"The reactivity of ultrathin transition metal oxide (TMO) films is closely related to so called *strong metal-support interaction* (SMSI) [10.212], which is mostly discussed in terms of a full or partial encapsulation of metal particles by a thin oxide layer stemming from a support.

A number of studies have addressed this problem. In particular, our own studies [10.33, 38, 40] of Pt nanoparticles deposited onto well-defined iron oxide surfaces showed encapsulation of the Pt surface by an iron oxide layer identified as FeO(111) monolayer film that is virtually identical to the one grown on a Pt(111) single crystal [10.213]. However, the FeO(111) film, initially stacked as an O–Fe bilayer, transforms at elevated oxygen pressures to an O-rich,  $\text{FeO}_{2-x}$ film with a trilayer (O–Fe–O) structure [10.37, 39]. Although the film stoichiometry implies Fe cations in the formal oxidation state 4+, i.e., unusual for iron compounds, DFT results showed that Fe ions in the trilayer structure are in the oxidation state 3+ due to a substantial electron transfer from the Pt(111) substrate. However, for brevity, we will use FeO and FeO<sub>2</sub> for the bi-layer and tri-layer structures, respectively. The CO oxidation reaction has been used as a probe reaction.

The reaction mechanism of CO oxidation, addressed by DFT using the model of a continuous  $FeO_2$  film, suggested CO reacting with the weakly bound, topmost oxygen atom in the O–Fe–O trilayer, thus forming CO<sub>2</sub> that desorbs leaving an oxygen vacancy behind [10.39]. The vacancy must be replenished by the reaction with molecular oxygen to complete the catalytic cycle. Our systematic study of reactivity of ultrathin oxide films formed from a number of different transition metals, such as Ru, Zn, Fe, and Mn, suggested the oxygen binding energy as a good descriptor for reactivity of the ultrathin oxide films [10.214] which may also be present at the rim of oxide islands.

Bao and coworkers have addressed the reactivity of FeO(111) and other TMO(111) monolayer structures on Pt(111) exposing the oxide/metal boundary [10.215-218]. On the basis of DFT calculations [10.216, 218], a Pt-cation ensemble was proposed, where coordinatively unsaturated TMO cations at the edges of TMO islands are highly active for O2 adsorption and dissociation. Dissociated oxygen binds to Pt at the TMO/Pt interface and is responsible for the facile CO oxidation. Note, however, that the calculations employed a simplified model, using a TMO ribbon, which does not account for the experimentally observed epitaxial relationships of oxide and Pt and related lattice mismatches, in turn resulting in various edge structures as observed [10.219]. More importantly, the oxide phase was modelled by the bilayer, i.e., O-TM-Pt(111), structure, which is not the structure relevant for technological CO oxidation reaction conditions, neither for FeO(111) nor for ZnO(0001) films on Pt(111) [10.28, 39]. Nonetheless, following these studies, the highest reactivity is expected to be on the rim of the FeO(111) islands, which are oxygen deficient and expose the unsaturated  $Fe^{2+}$  cations [10.215, 217, 218].

Recently, *Huang* and coworkers [10.220] have addressed the reactivity of FeO(111)/Pt(111) sur-

![](_page_40_Figure_1.jpeg)

Fig. 10.35 (a) CO oxidation rate as a function of the FeO(111) coverage on Pt(111). Reaction conditions: 10 mbar CO and 50 mbar  $O_2$ , balanced by He to 1 bar; 450 K. (b) Total  $CO_2$  production measured by TPD in low and high temperature (LT, HT) regions as a function of FeO coverage in original films

faces in the water gas shift reaction and preferential oxidation of CO in excess of H<sub>2</sub> using temperature programmed desorption (TPD) technique. It appears that the oxide structure is strongly affected via the reaction with water and hydrogen. A DFT study [10.221] performed on a more realistic model of FeO<sub>x</sub>/Pt(111), showed that, beyond terraces of the oxygen-rich FeO<sub>2-x</sub> phase, considered for a close film [10.39], also FeO<sub>2</sub>/FeO and FeO<sub>2</sub>/Pt boundaries may be involved in reactions. Finally, the metal–oxide synergy effect may also result from oxygen spillover from the oxide to the metal support.

We also studied the reactivity of FeO(111)/ Pt(111) films at submonolayer coverage both under near atmospheric and UHV-compatible pressures in order to bridge the pressure gap that may cause some controversy in results obtained by different groups [10.211]. We have shown that a much higher reactivity is, indeed, achieved by exposing an interface between the Pt support and the oxygen-rich  $FeO_{2-x}$  phase. Two synergetic effects concur: a low oxygen extraction energy at the  $FeO_2/Pt$  interface and a strong adsorption of CO on Pt(111) in its direct vicinity. Weak adsorption of CO on oxide surfaces levels out the (negligible) role of CO adsorption characteristics in the reaction over the closed oxide films, thus rendering the oxygen binding energy as the decisive parameter for reactivity of ultrathin oxide films [10.214].

Figure 10.35a shows the CO oxidation rate (measured by gas chromatography) over FeO(111)/ Pt(111) films at 450 K in the reaction mixture of 10 mbar CO and 50 mbar  $O_2$  (balanced by He to 1 bar) for different oxide coverages. (Note, that the initial rate was solely measured in order to neglect any deactivation effects). In the course of the reaction the initially grown FeO(111) islands transformed into the  $FeO_{2-x}$  islands in agreement with STM results of Fu et al. [10.217] The rate vs coverage plot revealed a maximum at  $\approx 0.4$  ML coverage. The rate is substantially (by a factor of 3.5) higher than obtained for a closed, monolayer film, which is, in turn, more active than the pristine Pt(111) surface, in full agreement with our previous studies [10.39]. Obviously, the oxide/metal interface provides reaction sites more active than those on the (interior) surface of FeO<sub>2</sub> islands.

More detailed experiments on FeO(111)/ Pt(111) films at sub-ML coverages using CO TPD as a function of oxide coverage, exposure, and preparation conditions revealed that  $CO_2$  production from CO oxidation came in two temperature regimes. The one at low temperature (LT, below 350 K) is very similar to that obtained on pristine Pt(111), whereas the reaction at high temperature (HT, 350–550 K) originates only on oxide covered surface.

Figure 10.35b depicts the total amounts of  $CO_2$  measured in six consecutive CO TPD spectra in

![](_page_41_Figure_1.jpeg)

Fig. 10.36 (a) Computational model of a sub-monolayer FeO<sub>x</sub> film on the Pt(111) surface. The nonequivalent oxygen sites are labeled 1–7: T–FeO (1),  $T_I$ -FeO<sub>2</sub> (2),  $T_S$ -FeO<sub>2</sub> (3), E-FeO/Pt (4),  $E_I$ -FeO<sub>2</sub>/Pt (5),  $E_S$ -FeO<sub>2</sub>/Pt (6), E-FeO<sub>2</sub>/FeO (7). Pt, O and Fe atoms are represented by *gray*, *red* and *blue spheres*, respectively. (b) Most stable CO adsorption configurations at the FeO<sub>2</sub>/Pt (*left*) and FeO<sub>2</sub>/FeO (*right*) boundaries depicted in panel (a). Pt, O, C and Fe atoms are represented by *gray*, *red*, *black*, and *blue spheres*, respectively. Reprinted with permission from [10.211]

the LT and HT regions, respectively, as a function of oxide coverage. The LT signal reversely scales with the oxide coverage, in full agreement with reaction taking place on uncovered areas of Pt(111). The observed linear relationship also suggests no (or negligible) oxygen spillover from FeO<sub>2</sub> islands onto the Pt(111) surface. In contrast, CO<sub>2</sub> production in the HT state goes through the maximum in the same manner as observed for the CO oxidation rate at near atmospheric pressures (Fig. 10.35a), thus providing compelling evidence that the enhanced activity must be attributed to the reaction at the interface between Pt(111) and FeO<sub>2</sub> trilayer.

Also, DFT calculations have been performed to estimate the thermodynamic stability of oxygen at a variety of alternative terrace and boundary sites, characteristic of Pt-supported FeO<sub>r</sub> film at sub-ML coverage. The computational model depicted in Fig. 10.36a represents an oxide coverage of 0.6 ML, with an equal proportion of FeO and  $FeO_2$ , accounting for the case of large  $FeO_x$  islands on the Pt(111) surface. It consists of embedded FeO<sub>2</sub> islands, with trilayer O-Fe-O structure, located primarily in the region of the so-called hcp lattice registry (O ions on-top of surface Pt atoms, Fe ions in the hollow sites), where the oxygen-rich film forms the most easily [10.37]. Conversely, bare FeO(111) is most stable in regions of fcc registry (both O and Fe ions in three-fold hollow sites of a Pt(111) substrate). The large unit cell contains also the region of a bare Pt(111) surface created by removing the oxide from regions of *top* registry (O ions in the hollow sites, Fe ions on-top of a surface Pt), where the stability of a  $FeO_x$  film is the lowest [10.37, 222].

While the oxygen extraction thermodynamics identified edge (E-FeO<sub>2</sub>/Pt and E-FeO<sub>2</sub>/FeO) sites as the most plausible candidates to react with CO (with a small preference for the latter), the very different characteristics of CO adsorption (2.05 vs 0.05 eV, respectively) clearly indicates that these two sites have a different efficiency for CO oxidation. Since CO binds only weakly to the FeO<sub>2</sub>/FeO boundary, the Eley–Rideal reaction mechanism is anticipated on these sites. Conversely, strong CO binding in the direct vicinity of the FeO2/Pt boundaries makes the Langmuir-Hinshelwood mechanism operative. Although in the latter case CO and O binding characteristics are close to those obtained on the bare Pt(111) surface, the FeO<sub>2</sub> oxide phase provides O atoms which do not suffer from the CO blocking effect which, otherwise, poisons the CO oxidation reaction on the bare Pt surface.

Certainly, for the rate enhancement to occur CO must adsorb sufficiently strongly, otherwise it desorbs intact before reaction with oxygen. Therefore, weakly adsorbing metal surfaces, such as Ag(111), do not show such effect as previously reported for ZnO(0001) films [10.223]. Accordingly, using oxygen binding energy as a principal descriptor for CO oxidation over ultrathin oxide films seems to be valid only for the systems exhibiting relatively weak CO adsorption which does not compete for oxygen adsorption sites. In the case of systems exposing a metal/oxide interface, the reactivity may be considerably enhanced by metals strongly adsorbing CO like Pt. In such cases, the model of overlapping states [10.224] seems to be fairly predictive, suggesting high activity when the desorption profiles for each individual molecule reacting at the surface overlap.

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#### 10.4.4 Olefin Hydrogenation over Pd/Fe<sub>3</sub>O<sub>4</sub>(111)

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Real catalytic processes often require small amounts of some additives (promoters), such as e.g., alkali metals or halogens [10.100], that ensure high catalytic activity and selectivity. The role that these compounds play at a microscopic level remains unclear for most of the known catalytic systems in operation. One of the most important coadsorbates, particularly in hydrocarbon chemistry, is carbon resulting from decomposition of the reactants. Accumulation of carbon was recognized to considerably affect the activity and the selectivity in hydrocarbon conversions promoted by transition metals [10.226]. In our studies, by comparing the hydrogenation activity of clean and C-containing Pd nanoparticles we addressed the underlying microscopic mechanisms of C-induced changes in the catalytic performance for hydrogenation of olefins [10.227-229].

Hydrogenation rates of cis-2-butene over clean and C-containing Pd nanoparticles supported on Fe<sub>3</sub>O<sub>4</sub>(111)/Pt(111) film are shown in Fig. 10.37a. Pd nanoparticles were saturated first with deuterium to form both surface and subsurface D species [10.230] and then short pulses of cis-2-butene were applied. Clean Pd nanoparticles exhibit high hydrogenation activity for an initial short period of time (a few butene pulses), after which it drops to zero. In contrast, if carbon was deposited on Pd nanoparticles before the reaction, a sustained hydrogenation rate was observed. Using CO as a probe molecule for different adsorption sites, it can be shown that deposited carbon modifies the low-coordinated site such as edges and corners [10.230]. However, it is not clear whether carbon resides on the surface or might penetrate into the subsurface region as predicted theoretically [10.231]. This effect demonstrates the exceptional importance of carbon for olefin hydrogenation, which can be carried out in a truly catalytic fashion for many turnovers, only on Ccontaining Pd nanoparticles.

The role of carbon in promotion of sustained hydrogenation was rationalized by employing transient molecular beam experiments and resonant nuclear reaction analysis (rNRA) for hydrogen depth profiling. First, we obtained the first direct experimental evidence that the presence of H(D) absorbed in the Pd particle volume is required for olefin hydrogenation, particularly for the second half-hydrogenation step [10.227], in agreement with previous experimental evidences [10.232]. This result explains the high initial hydrogenation rates, observed on the clean particles fully saturated with D, and vanishing hydrogenation activity in steady state because of the depletion of the subsurface D reservoir (Fig. 10.37a). Apparently, the inability to populate subsurface D sites arises from hindered D subsurface diffusion through the surface covered with hydrocarbons. Further, it was shown that even a submonolayer coverage of carbon significantly affects the H(D) depth distribution in Pd particles [10.227]. Based on these observations, and on the analysis of the hydrogenation kinetics [10.229], we attribute the sustained hydrogenation activity to facilitation of H(D) diffusion into the particle volume by deposited carbon.

The proposed mechanism was confirmed both theoretically and experimentally [10.233, 234]. Computational studies on Pd nanoclusters demonstrated that deposited carbon dramatically enhances the hydrogen diffusion rate into subsurface, mainly due to a local elongation of Pd-Pd bonds and a concomitant lowering of the activation barrier [10.233]. This dramatic reduction of the activation barrier can account for the experimentally observed unusual promotion of sustained hydrogenation activity by carbon. In contrast, the lateral rigidity of the extended Pd(111) surface was predicted to hinder this effect, in agreement with experimental observations [10.228]. The results demonstrate the conceptual importance of atomic flexibility of sites near particle edges, which, in contrast to intrinsically rigid regular single crystal surfaces, play a crucial role in H subsurface diffusion on Pd.

Finally, we provided direct experimental evidence for a faster subsurface H diffusion through C-modified low-coordinated surface sites on Pd nanoparticles by probing the diffusion rate via  $H_2 + D_2 \rightarrow HD$  exchange in different temperature regimes [10.234]. It was previously shown [10.230] that the formation of HD can occur either via recombination of two surface H and D species or an involvement of subsurface H or D species. The latter pathway dominates at low temperatures between 200 and 300 K. Our experimental results are consistent with the scenario implying that one subsurface atom (H or D) recombines with a surface-adsorbed atom to form HD. In the case of slow subsurface H(D) diffusion, the formation rate of subsurface species will be the limiting step in HD production, and can, therefore, be addressed by probing the rate of isotopic scrambling.

Figure 10.37c shows the steady state HD formation rates at 260 and 320 K on clean and Cmodified Pd nanoparticles. C-modification of the particles edges was found to affect the HD formation rate in a dramatically different way for two reaction temperatures: whereas at 320 K preadsorbed C reduces the overall reaction rate by about  $30^{\circ}$ , the reaction rate *increases* by about  $100^{\circ}$  at 260 K on the C-modified particles. The decreased HD formation rate at 320 K, where HD formation is dominated by the recombination of the surface H and D species [10.230], can be rationalized as a consequence of the blocking of surface adsorption sites by carbon. Interestingly, even though a part of the surface is blocked by carbon, the HD formation rate is significantly increased at 260 K,

where desorption involves at least one subsurface H(D) species. This effect can be explained only by the higher formation rate of the subsurface H(D) species on the C-modified particles, resulting in a higher steady state concentration.

Such insight allowed us to identify an exceptionally important role of carbon in hydrogenation chemistry on nanostructured catalysts that was previously not clearly appreciated. According to our model, small amounts of carbon modify the lowcoordinated surface site of Pd nanoclusters (edges, corners), thus allowing for effective replenishment of subsurface H in steady state and enabling sustained hydrogenation. These results also highlight the crucial role of subsurface H diffusion, which is a strongly structure-sensitive process on Pd surfaces, in hydrogenation of the olefinic bond. Computational studies suggest that the atomic flexibility of the low-coordinated surface sites is an important structural feature that is responsible for easy subsurface diffusion of H under operation condition."

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#### 10.5 Oxide Films Beyond UHV

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"The investigations discussed so far were limited to systems studied under UHV conditions which immediately poses the question how these results relate to oxide systems at ambient conditions such as an aqueous environment. In the following we illustrate how such well-defined systems prepared under UHV conditions can be used to study the properties of the oxide surfaces under ambient conditions.

#### 10.5.1 Alkaline Earth Oxides, Iron Oxides and Silica Out of UHV into Solution

## Stability and Dissolution of Thin Oxide Films in Aqueous Environment

A variety of technologically important processes, such as catalyst preparation by wet impregnation, involve processes at the liquid/oxide interface. Aiming at the investigation of such processes using well-defined thin oxide films the system has to be stable under the specific environmental conditions of interest. For surface science investigations in particular, it is desirable that the structural order is maintained. Since the chemical properties of (most) oxide thin films are similar as those of the corresponding bulk analogues, their stability and dissolution behavior is expected to follow the same trends. Dissolution rates for oxide thin film samples can be derived from the measured decrease of film thickness upon exposure to aqueous solution, which can straightforwardly be determined from the intensities of the oxide and substrate XPS or AES (Auger electron specttroscopy) emissions.

XP spectra (O 1s and Si 2p regions) taken after exposing bilayer SiO<sub>2</sub>/Ru to deionized water at 90 °C, and NaOH(aq) at 25 °C for various times are displayed in Fig. 10.38a [10.204]. Clearly, deionized water (pH 7) does not affect the film structure to any significant extent, even at elevated temperature. While a small shift of all silica-related XP peaks to higher BE, which reflects a slight change in the electronic structure of the system (band bending), is noted, neither the Si 2p nor the O 1s peaks suffer any loss of intensity. In

![](_page_44_Figure_1.jpeg)

**Fig. 10.37a,b** Hydrogenation rate of *cis*-2-butene at 260 K over clean (a) and C-precovered (carbon adsorbed at Pd nanoparticle edges) (b) model catalysts Pd/Fe<sub>3</sub>O<sub>4</sub>/Pt(111). (c) The steady state HD formation (H<sub>2</sub> + D<sub>2</sub>  $\rightarrow$  2HD) rates obtained on the pristine and C-precovered Pd nanoparticles supported on Fe<sub>3</sub>O<sub>4</sub>/Pt(111) at 260 and 320 K. Reprinted (adapted) with permission from [10.234]. Copyright (2011) American Chemical Society. (d) Proposed reaction mechanism of olefin hydrogenation on Pd nanoparticles

![](_page_45_Figure_1.jpeg)

Fig. 10.38 (a) Evolution of O 1s (*left*) and Si 2p (*right*) XP spectra of SiO<sub>2</sub>/Ru(0001) samples as a function of time of exposure to (*top*) deionized water at 90 °C, and (*bottom*) 0.1 M NaOH at 25 °C. (b) Peak intensity ratios of Si 2p relative to Ru 3d for bilayer SiO<sub>2</sub>/Ru samples exposed to aqueous NaOH solutions at pH 13 and various temperatures (*left*) and varying pH at 90 °C (*right*) as a function of time spent within the aqueous environments. Reprinted from [10.204], with permission from Elsevier. (c) *Left*: Dissolution of MgO(001)/Ag(001) films (initial thicknesses corresponding to the values at time = 0 s) in various environments plotted as MgO film thickness vs. time of exposure to solutions; *black*: 0.01 M NaOH solution (pH 12), *blue*: Millipore water (pH 6), *red*: 0.01 M HCl solution (pH 2). (c) *Right*: Dissolution of MgO(001)/Ag(001) in 0.01 M NaOH. Reprinted from [10.235], with permission from Elsevier. (d) Air-STM images of Fe<sub>3</sub>O<sub>4</sub>(111)/Pt(111) taken after transfer from UHV to air (*left*), after 60 min exposure to 0.1 M HCl, pH 1 (*middle*) and after 60 min exposure to NaOH<sub>aq</sub>, pH 10 (*right*)

contrast, the intensity of both peaks decreases significantly, even at 25 °C, when the silica bilayer is exposed to alkaline media (NaOH, pH 13). The equal relative signal intensity loss of Si and O peaks observed with time of exposure allows to conclude that, in accordance with general experience, the dissolution process in alkaline media can be described as the OH<sup>-</sup> catalyzed hydrolysis of SiO<sub>2</sub> (SiO<sub>2</sub> + 2H<sub>2</sub>O  $\rightarrow$  H<sub>4</sub>SiO<sub>4</sub>). One can further state that the bilayer SiO<sub>2</sub>/Ru films resemble the dissolution behavior of other, more abundant forms of silica (quartz, amorphous silica), which are found to be practically insoluble in the neutral pH range, and more strongly soluble in alkaline conditions. From more systematic studies of dissolution as a function of temperature and pH (Fig. 10.38a, lower part) it is clear that removal of SiO<sub>2</sub> from the sample shows a preference for larger values of both parameters, which is also qualitatively consistent with the behavior noted from bulk-phase silica analogues [10.236]. The dissolution rates for the thin film sample can be modeled by the general silica dissolution rate model derived by *Bickmore* et al. [10.236], which accounts for variations in pH, temperature, and the coverage of neutral ( $\theta_{Si-OH}$ ) and deprotonated ( $\theta_{Si-O-}$ ) silanols. Because the silica film is hydrophobic and lacks significant initial silanol coverage, the latter two contributions can be neglected and the rate equation simplifies to

$$\frac{dSi}{dt}\frac{mol}{s} = e^{6.7 \pm 1.8} T e^{\frac{-77.5 \pm 6.0}{RT}} [OH^{-}].$$

A comparison of the dissolution rates predicted from that relation to those estimated on the basis of the initial rates of Si XPS peak attenuations from the thin films shows good agreement between the model and the experiment [10.204]. From this, it is concluded that dissolution of the film in alkaline media is initiated by  $OH^-$  attack at Si centers. Note that this leads to rupture of siloxane bonds. Thus, the initial step in the dissolution process can qualitatively be described by models that are similar to those used to explain electron-assisted hydroxylation of the silica film (Fig. 10.28f). In general, the silica bilayer films were found to be stable (i.e., negligible dissolution rates observed) at room temperature in acidic and neutral aqueous solutions, and in alkaline media up to pH 10 [10.204].

MgO is a basic oxide (point of zero charge (PZC) in the pH10 range) and therefore expected to be more stable in alkaline media than in neutral and acidic environment [10.237]. Results of dissolution experiments performed with MgO(001)/Ag(001) thin films are presented in Fig. 10.38b, where the variation of MgO film thickness as a function of time is displayed for exposure to acidic (pH2, 0.01 M HCl), alkaline (pH12, 0.01 M NaOH) and close to neutral (pH 6, Millipore water) environments, respectively [10.235]. The data shown in Fig. 10.38b is consistent with the expected faster dissolution of MgO in acidic media. In fact, in 0.01 M HCl solution the dissolution is so fast that a 11 ML thick film was completely dissolved within the first 5 s of exposure. The dissolution rate is smaller at pH 6; however, even under these conditions a 13 ML thin MgO film was completely dissolved within 5 s of exposure. During the same period, only 3 ML MgO were dissolved from the MgO sample upon exposure to alkaline (pH 12) solutions. For the latter, the dissolution behavior was studied for prolonged exposures (up to 90 min), the results of which show that the dissolution is initially fast and considerably slows down with time, until a stable surface state is obtained after 20-30 min of exposure. This suggests the formation of a brucite  $(Mg(OH)_2)$ like passivating surface layer during exposure to alkaline solution, for which dissolution rates are considerably smaller than for MgO [10.238]. Because of the partial dissolution, and transformation of the surface layers into a hydroxide, MgO films exposed to alkaline media are subject to strong restructuring. Even if the crystallinity of the films can partially be recovered by annealing at elevated temperature, the initial structure of the MgO(001) films cannot be restored [10.235].

Iron oxides are, according to the corresponding Fe-water Pourbaix diagram, stable in aqueous solutions in a wide range of pH. Thus, it is not surprising that also thin iron oxide films are very stable in aqueous solutions. As an example, STM images taken in air from Fe<sub>3</sub>O<sub>4</sub>(111)/Pt(111) films, which have been prepared in UHV and subsequently transferred to air ambient and exposed to aqueous solutions (pH 1, 0.1 M HCl and pH 10,  $NaOH_{aq}$ ) for 1 h, are shown in Fig. 10.40c [10.239, 240]. These images reveal that the island-terracestep structure of the thin film remains intact. Furthermore, the step edges run straight along the crystallographically preferred directions and the terraces are atomically flat. XPS taken from the exposed films indicates a slight oxidation of the surface, but this does obviously not lead to structural modifications. Both, Fe<sub>3</sub>O<sub>4</sub>(111)/Pt(111) and bilayer silica films (and to a limited extent also MgO(001)/Ag(001)) are therefore well suited for further investigations of processes involving oxide-liquid interfaces."

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#### Surface Science Approach to Catalyst Preparation: Pd-Fe<sub>3</sub>O<sub>4</sub> as an Example

In Sect. 10.4.4 we have already shown that Pd nanoparticles deposited on a Fe<sub>3</sub>O<sub>4</sub>(111) surface are good catalysts for hydrogenation reactions. The system discussed above was prepared by physical vapor deposition of Pd atoms onto the oxide surface under UHV conditions. However, almost all supported catalysts employed industrially are prepared by wet-chemical methods such as impregnation, deposition-precipitation, spreading, and ion exchange [10.74]. The first step in a commonly applied wet-chemical catalyst preparation procedure consists of the interaction of the support with precursor solutions that contain the metal component in the form of salts or complexes. This is followed by drying, calcination and reduction steps, which are necessary to transform the adsorbed metal precursor into the catalytically active phase. Among other approaches, thin oxide films have recently been used to model typical catalyst preparation procedures with flat, single-crystalline substrates [10.235, 239–242].

With Fe<sub>3</sub>O<sub>4</sub>(111)/Pt(111) as support, the preparation of supported Pd nanoparticles using PdCl<sub>2</sub> as a precursor has been studied [10.239, 240]. The speciation of PdCl<sub>2</sub> in aqueous solutions has been the subject of intense research in the past. In strongly acidic conditions, the tetrachloro complex PdCl<sub>4</sub><sup>2-</sup> is the most abundant species (Fig. 10.39a). Upon hydrolysis, the chlorine ligands are gradually replaced by aqua or hydroxo ligands, leading finally to Pd(OH)<sub>4</sub><sup>2-</sup> species in strongly basic medium [10.243, 244]. Neutral Pd complexes of the kind [PdCl<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] are formed at an intermediate stage of hydrolysis. These complexes

![](_page_47_Figure_1.jpeg)

**Fig. 10.39** (a) pH-dependent speciation of  $PdCl_2$  in aqueous solution. (b) STM images ( $75 \times 75 \text{ nm}^2$ ) of Pd nanoparticles on  $Fe_3O_4(111)$  obtained by exposure of freshly prepared  $Fe_3O_4(111)/Pt(111)$  to  $PdCl_2$  solutions of different pH followed by drying and annealing at 600 K in UHV. (c) Schematic representation of the adsorption of Pd-complexes on oxide surfaces in acidic (pH below the PZC of the oxide) and alkaline media (pH above the PZC of the oxide)

are most probably responsible, because of their tendency for polymerization ( $\rightarrow$  polynuclear Pd-hydroxo complexes, PHC), for the formation of colloidal particles [10.245], seen with the appearance of the dark brown color of the Pd solution (Fig. 10.39a). The pH at which formation of PHC's sets in can be slightly varied by changing the Pd<sup>2+</sup> and Cl<sup>-</sup> concentration. The strong influence of the solution pH on the Pd loading and the particle morphology is demonstrated by means of the STM images displayed in Fig. 10.39b. These images were obtained following exposure of the Fe<sub>3</sub>O<sub>4</sub>(111) films to precursor solutions (5 mM PdCl<sub>2</sub>) exhibiting different pH (as indicated in Fig. 10.39b), and subsequent thermal treatment at 600 K in UHV, which transforms the adsorbed Pd precursor into Pd particles. First, the samples prepared with the low pH solutions (pH 1.3–2.5), where the influence of PHC's can be excluded, are considered. The trend toward higher Pd loading and slightly increasing Pd particle size with increasing pH is obvious and in agreement with results obtained for similar preparations carried out with powder samples [10.246]. Within the strong electrostatic adsorption model (Fig. 10.39c, top), which seems to be applicable for the given conditions (negatively charged precursor and positively charge support surface, PZC of Fe<sub>3</sub>O<sub>4</sub> is  $\approx$  pH 6.5) the suppression of Pd precursor adsorption at low pH, which results in low Pd loading, is typically explained by the lowering of the equilibrium adsorption constant as an effect of the higher ionic strength of the strongly acidified precursor solution [10.247].

While small and homogeneously distributed Pd particles are formed following exposure to the low pH solutions, a high Pd loading and large Pd particles are obtained if the pH 4.7 precursor solution is applied (Fig. 10.39b). At first glance, this result might be related to the adsorption of colloidal particles present in the precursor solution. However, deposited particles could not be identified by STM directly after deposition. Therefore, a different adsorption mechanism for the Pd precursor needs to be considered at this pH conditions. Since at pH4.7 the Fe<sub>3</sub>O<sub>4</sub> surface is essentially uncharged and a considerable fraction of the solution species is charge-neutral, a strong chemical interaction via hydrolytic adsorption of the precursor complexes could be the reason for the high Pd loading. With the basic pH 10 precursor solution the Pd loading decreased again and a particle size distribution that is more homogeneous as compared to the one obtained with the pH4.7 precursor solution was obtained. Since both the oxide surface and the solution complexes are negatively charged in this case, electrostatic adsorption is believed to play a negligible role and the adsorption of Pd occurs mainly via hydrolytic adsorption of the Pd-hydroxo complexes on the surface hydroxyl groups (Fig. 10.39c, bottom). Copyright Springer [10.242].

More detailed studies regarding the stepwise decomposition of the adsorbed precursors into metallic nanoparticles were conducted with samples prepared by exposure to pH1.3 and pH10 precursor solutions, respectively [10.239, 240]. As an example, the results obtained with the alkaline precursor solution

![](_page_48_Figure_1.jpeg)

Fig. 10.40 (a) STM images  $(100 \times 100 \text{ nm}^2)$  and (b) corresponding Pd 3d XP spectra of a Fe<sub>3</sub>O<sub>4</sub>(111)/Pt(111) thin film surface acquired after exposure to Pd precursor solution (5 mM PdCl<sub>2</sub>, pH 10) and subsequent drying (RT, *top*), after drying at 390 K (*middle*), and subsequent heating to 600 K (*bottom*). (c) IRA spectrum taken after adsorption of CO at 80 K on a Pd/Fe<sub>3</sub>O<sub>4</sub>(111) model catalyst prepared by exposure to pH 10 PdCl<sub>2</sub> precursor solution. (d) STM image  $(100 \times 100 \text{ nm}^2)$  of Pd/Fe<sub>3</sub>O<sub>4</sub>(111) prepared by physical vapor deposition of Pd onto a Fe<sub>3</sub>O<sub>4</sub>(111) surface modified by treatment with NaOH solution. After [10.242]

are reproduced in Fig. 10.40a (STM) and Fig. 10.40b (XPS) [10.240]. An STM image of the  $Fe_3O_4(111)$  surface following exposure to the precursor solution (2 mM PdCl<sub>2</sub>, pH10) and subsequent water rinsing and drying shows an apparently *clean* oxide surface with the typical morphological features of  $Fe_3O_4(111)$  (Fig. 10.40a, top). However, the corresponding XPS spectrum confirms the presence of Pd on this surface (Fig. 10.40b, top). Obviously, the adsorbed precursor complexes are homogeneously distributed across the surface and cannot be individually resolved in STM. The two Pd  $3d_{5/2}$  photoemission signals identified at

337.8 and 336.5 eV BE can be assigned to Pd-hydroxo and PdO species, respectively. It has to be mentioned that the high BE component was found to be sensitive to x-ray irradiation, and the PdO component identified at this stage of the preparation results most probably from x-ray induced decomposition of the Pd-hydroxide into PdO. Only mild drying at 390 K completely changes the surface morphology, which displays small particles with an average diameter of 2.5-3 nm (Fig. 10.40a, middle). This morphological change is accompanied by an almost complete transformation of the adsorbed Pdhydroxide precursor into PdO, as deduced from the loss of the high BE component in XPS and the concurrent increase of the 335.9 eV feature (Fig. 10.40b, middle). Finally, fully reduced Pd particles (particle diameter: 3-7 nm) are found after further thermal treatment at 600 K (Fig. 10.40a,b, bottom). These particles contain some carbon contamination remaining from the preparation process, which can be eliminated by oxidation at 500 K in  $1 \times 10^{-6}$  mbar O<sub>2</sub>. Subsequent reduction in CO atmosphere restores the metallic state, which then presents CO-IRAS signatures typical for supported Pd nanoparticles (Fig. 10.40c) with two bands arising, respectively, from on-top bound  $(2105 \text{ cm}^{-1})$  and bridgebonded CO (1990 cm<sup>-1</sup>) [10.248]. Alternatively, the final reduction step was performed in H2 instead of CO atmosphere, which led to the formation of bimetallic Pd-Fe particles due to strong metal support interaction (SMSI). This modification can be easily understood on the basis of the catalytic action of Pd in providing H atoms for reduction of the Fe<sub>3</sub>O<sub>4</sub> support via H<sub>2</sub> dissociation and H spill-over. Iron atoms from the reduced support then migrate into the Pd particles.

An important question to ask at this point is whether or not the morphology of a model catalyst prepared by wet-chemical procedures as described above differs from that of a corresponding model catalyst prepared exclusively in UHV. In other words, does the nature of the precursor (single atoms in UHV vs. metal complexes in solution) or the support properties (clean surface in UHV vs. a surface modified by exposure to precursor solution) affect the properties of the activated model catalyst? In order to answer this question two additional Pd/Fe<sub>3</sub>O<sub>4</sub>(111) model catalysts were prepared: One, where Pd was deposited onto a clean Fe<sub>3</sub>O<sub>4</sub>(111) support in UHV by vapor deposition (Pd/Fe<sub>3</sub>O<sub>4</sub>(UHV), Fig. 10.40d), and another one, where Pd was deposited by vapor deposition onto a  $Fe_3O_4(111)$  surface following a treatment with NaOH (pH 12) solution  $(Pd/Fe_3O_4(hydr), Fig. 10.42b,e)$ . The NaOH treatment was applied in order to achieve a surface functionality comparable to the solution deposition experiment. Inspection of the corresponding STM images (Fig. 10.40d,e) reveals differences between the two samples with respect to the arrangement of the Pd particles and the particle size distribution. While the Pd particles are uniform in size and arranged in an almost perfect hexagonal array on the clean Fe<sub>3</sub>O<sub>4</sub>(111) surface, the surface order is lost on the pretreated Fe<sub>3</sub>O<sub>4</sub> surface and a deviation from the normal particle size distribution is apparent. Most notably, the morphology of the  $Pd/Fe_3O_4(hydr)$  sample (Fig. 10.40e) closely resembles that of the model catalyst prepared by deposition of Pd from the pH 10 precursor solution (Fig. 10.40a, bottom). This finding suggests that in the present case the morphology of the activated model catalyst is mainly governed by the interfacial properties, and not by the nature of the precursor. The more heterogeneous sintering of Pd particles on the modified surfaces is attributed to the presence of hydroxyl groups and the existence of a variety of adsorption sites with differing Pd adhesion properties [10.240], Copyright Springer [10.249].

#### 10.5.2 Water/Silica Interface

To date, most of the research on silica bilayers has been performed in idealized ultra-high vacuum environments. These conditions provide a high degree of experimental control which enables unambiguous structural assessment. Yet real world applications of silica and its derivatives demand higher pressures and temperatures and occur under ambient condition. Recent research on silica bilayers beyond ultra-high vacuum addresses these practical considerations by bridging the gap between UHV and ambient.

In order to bridge such gap, the structure of silica has been investigated with high-resolution liquid atomic force microscopy (AFM). Silica films are grown in UHV and subsequently transferred through ambient to the liquid environment (400 mM NaCl solution). Figure 10.41 shows images of the bilayer silica structure attained with ultra-high vacuum STM and high resolution liquid-AFM [10.250]. The low-temperature UHV STM images exhibit atomic resolution of the silica structure while the resolution of the room temperature liquid-AFM images allows to identify the ring structures. The structures appear remarkably similar as confirmed quantitatively from pair distribution functions of the ring center positions. These results show that the silica film is structurally robust against ambient and aqueous conditions; this result is consistent with the conclusions of the previous study which found the silica bilayer film to be exceptionally stable against hydroxylation [10.199]. In contrast, many UHV surface structures are not stable under ambient conditions due to unsaturated bonds [10.198, 235]. The stability of the silica bilayer makes it an optimal playground to test the resolution of liquid AFM as the amorphous structure circumvents the common challenge of distinguishing between true atomic resolution and lattice resolution [10.251]. Furthermore, establishing the stability of the silica bilayer under ambient conditions opens the door to future device applications.

![](_page_50_Figure_1.jpeg)

Fig. 10.41a-d An amorphous silica bilayer film with atomic resolution of silicon atoms by STM in UHV (a) and ring resolution by liquid-AFM in (d). Both images have a scan frame of  $5 \text{ nm} \times 5 \text{ nm}$ . *Red, orange,* and *yellow measurement bars* show examples of ring center–center distances for the first three families of ring neighbors identified in the amorphous silica bilayer. Several individual rings are marked in each image. (d) Reprinted from [10.250], with the permission of AIP Publishing. The measurement in (a) has been obtained with a custom-made low temperature ultra-high vacuum STM shown in (b) while (d) has been taken with a commercial liquid-AFM photographed in (c)

![](_page_50_Figure_3.jpeg)

**Fig. 10.42** (a) Top and side view of a boron nitride layer in comparison to the silica bilayer (b) and (c). In contrast to graphene both shown 2-D materials are wide band-gap insulators. (d) Schematic of the transfer procedure: silica bilayer on ruthenium substrate, spin coating of system with polymethyl methacrylate (PMMA) layer, mechanical exfoliation of PMMA, silica adheres to PMMA layer, silica supported on PMMA layer, placing the PMMA-supported silica layer on clean Pt(111) substrate, subsequent heat treatment, after PMMA removal, silica is supported on Pt(111) substrate. Reprinted (adapted) with permission from [10.57]. Copyright (2016) American Chemical Society

#### 10.5.3 Peal-Off Experiments with Silica Films

Silica bilayers are an ideal candidate material for inclusion in two-dimensional nanoelectronic heterostructures due to its insulating character and high degree of structural integrity under ambient conditions [10.252]. Novel nanoelectronic heterostructure devices are designed with tailored properties by bottom-up production which combines two-dimensional insulating, semiconducting, and conducting materials. Numerous options exist for two-dimensional semiconductors, yet to date hexagonal boron nitride is the most widely used two-dimensional insulator. Silica bilayers are wide band-gap insulators with band gaps on the order of 6.5-7.3 eV [10.253, 254] and provide a two-dimensional analog of the SiO<sub>x</sub> insulating layer used in the semi-conductor industry. In order to use bilayer silica for nanoelectronic devices, transfer of the bilayer from the growth substrate is necessary. This procedure has been sketched in Fig. 10.42. Silica bilayers

are grown on Ru(0001) in vacuum and subsequently moved to ambient [10.57]. The silica bilayer has been successfully transferred to a new Pt(111) substrate via polymer assisted mechanical exfoliation. The transferred sample is heated to remove polymer residue and the structural integrity of the silica film is maintained throughout the process. With this achievement, silica has been added to the toolbox of two-dimensional materials for nanoelectronics, bridging the gap between fundamental structural studies and technological applications.

#### **10.6 Conclusions**

In this chapter we have compiled a range of experimental results to address some of the important questions that need to be understood if aiming at an atomistic understanding of chemical processes at oxide surfaces. The experiments described here use well-defined, single crystalline oxide films as model systems, which were proven to be suitable to address the properties of oxide surfaces and allow for their characterization with the rigor of modern surface science methodology. The basis for the atomistic understanding is a detailed knowledge of the structural properties of the system at hand. Using some selected systems, we have shown how the machinery of modern surface science can be used to determine the structural properties of oxide surfaces. It is important to emphasize the increased complexity of oxide surface structures in comparison to metals and we have addressed some of these such as surface termination and defect structures, among others. Oxides cover a wide range of chemical and physical materials properties from wide band-gap insulators to metallic systems. We provide some examples how the properties of the oxides can be tuned focusing on the ability to control charge transfer processes at the surface of oxides using the film thickness or appropriate doping of the system as exemplified for alkaline earth oxide surfaces. Oxide surfaces play a pivotal role in heterogeneous catalysis not only as support for transi-

#### References

tion metal nanoparticles but also as catalytically active phases. In addition, alterations of the surface structure may occur by reaction of the surface with gas phase species not necessarily being educts of the chemical reaction. To this end as well as because of its great importance for a variety of technological and natural processes, the interaction of water with oxide surfaces is of great interest. We have compiled a variety of experimental results to indicate the level of information that may be obtained. Furthermore, as an example for transition metal oxide surfaces we allude to vanadia in order to show how a detailed characterization of surface species on model systems can help to gain insight that may also be transferred onto more complex powder systems. Apart from these studies we demonstrate the ability to study the kinetics of chemical reactions on such model systems in great detail using molecular beam techniques. The model systems also lend themselves to studies at elevated pressures to learn about modifications of the surface under those conditions, which may have direct consequences for the chemical reactivity of the system. Finally, we discuss the possibility to transfer these systems prepared under UHV conditions into the ambient, exemplifying this by discussing the growth of metal nanoparticles from solution as well as the ability to peal silica films off the supporting metal surface.

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#### **Hans-Joachim Freund**

Chemical Physics Dept. Fritz Haber Institute of the Max Planck Society Berlin, Germany freund@fhi-berlin.mpg.de

![](_page_60_Picture_18.jpeg)

Hans-Joachim Freund received his PhD (1978) and his habilitation (1983) from the University of Cologne. 1983, he became Associate Professor at Erlangen University and in 1987 Professor at Bochum University. In 1995, he accepted a position as scientific member and director of the Department of Chemical Physics at the Fritz-Haber-Institut der Max-Planck-Gesellschaft in Berlin. He serves as Honorary Professor of five universities. He received several national and international awards.

#### **Markus Heyde**

Chemical Physics Dept. Fritz Haber Institute of the Max Planck Society Berlin, Germany heyde@fhi-berlin.mpg.de

![](_page_60_Picture_22.jpeg)

Markus Heyde heads the Scanning Probe Microscopy group in the Department of Chemical Physics at the Fritz-Haber-Institute. His research is focused on high-resolution local structure measurements on model systems for heterogeneous catalysis. Well-defined crystalline and amorphous oxide thin film systems are characterized by atomic resolution microscopy to gain insight into the chemical reactions taking place at these surfaces.

![](_page_60_Picture_24.jpeg)

#### Helmut Kuhlenbeck

Chemical Physics Dept. Fritz Haber Institute of the Max Planck Society Berlin, Germany kuhlenbeck@fhi-berlin.mpg.de Helmut Kuhlenbeck studied physics at the University of Osnabrück. In 1995, he finished the habilitation procedure at the University of Bochum. He has been a work group leader at the Chemical Physics department of the Fritz Haber Institute in Berlin since 1996. His activities are focused on areas related to structural studies and spectroscopy of chemical processes on well-ordered oxide surfaces.

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#### Niklas Nilius

Institut für Physik Carl von Ossietzky Universität Oldenburg Oldenburg, Germany niklas.nilius@uni-oldenburg.de Niklas Nilius studied physics and received his PhD in the group of H.-J. Freund for investigating the optical properties of individual nanoparticles. In 2002/2003, he worked as a postdoc with W. Ho on monatomic chains artificially assembled from single metal atoms. He has held a professorship at Oldenburg University since 2013, where he develops oxide model systems for photovoltaic and photochemical applications.

#### **Thomas Risse**

Institute of Chemistry and Biochemistry Physical and Theoretical Chemistry Freie Universität Berlin Berlin, Germany risse@chemie.fu-berlin.de

![](_page_61_Picture_7.jpeg)

Thomas Risse received his Doctorate in Physical Chemistry from Ruhr-Universität Bochum. From 1997 until 2010 he was staff scientist at the Fritz Haber Institute, with an interlude of 1 year as a postdoc at UCLA. In 2010 he became Professor of Physical Chemistry at Freie Universität Berlin. He is interested in ESR spectroscopy and its application to surfaces and spin labeled proteins.

#### Swetlana Schauermann

Institut für Physikalische Chemie Christian–Albrechts–Universität zu Kiel Kiel, Germany

![](_page_61_Picture_11.jpeg)

Swetlana Schauermann studied chemistry and received her PhD (2005) in the group of H.-J. Freund investigating heterogeneously catalyzed reactions at the atomistic level. Between 2006 and 2007, she was a postdoctoral fellow with R.M. Lambert (Cambridge University) and C.T. Campbell (University of Washington).She has been a professor at Kiel University since 2015. Her current research is focused on the kinetics of complex surface reactions and thermodynamics of gas–surface interactions.

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#### Thomas Schmidt

Chemical Physics Dept. Fritz Haber Institute of the Max Planck Society Berlin, Germany (BESSY II)

Helmholtz-Zentrum Berlin für Materialien und Energie Berlin, Germany thomas.schmidt@fhi-berlin.mpg.de Thomas Schmidt studied physics at the University of Hanover, where he received his PhD in 1994. After postdoc positions in Clausthal, ELETTRA (Trieste), and Würzburg, he became a group leader at the FHI in 2008. Using XPEEM, XPS, XEXAFS, LEEM, and LEED he investigates the growth and properties of ultrathin oxide films supported by metal single crystals.

## D

#### Shamil Shaikhutdinov

Chemical Physics Dept. Fritz Haber Institute of the Max Planck Society Berlin, Germany shaikhutdinov@fhi-berlin.mpg.de Shamil Shaikhutdinov has received his PhD (1986) from the Moscow Institute of Physics and Technology. He has worked at the Boreskov Institute of Catalysis (Novosibirsk) and as a postdoctoral fellow in Germany and France. Since 2004, he has been leading the group Structure and Reactivity in the Fritz-Haber Institute (Berlin). His research interest is focused on understanding of the atomic structure and surface chemistry of functional materials.

#### Martin Sterrer

Institute of Physics University of Graz Graz, Austria martin.sterrer@uni-graz.at

![](_page_61_Picture_24.jpeg)

Martin Sterrer received his PhD in Physical Chemistry from TU Vienna. In 2003 he joined Professor Freund's department as a postdoc and later headed the Catalysis and Laser Spectroscopy group in the department. In 2014, he moved to University of Graz, where he is now Professor of Experimental Physics and Head of the Surface Science group, working on model catalysis, solid–liquid interfaces and adsorption structures of large organic molecules.