

The Surface Science of Catalysis and More, Using Ultrathin Oxide Films as Templates: A Perspective

Hans-Joachim Freund*

Fritz-Haber-Institut der Max-Planck Gesellschaft, Department of Chemical Physics, Faradayweg 4-6, 14195 Berlin, Germany

ABSTRACT: Surface science has had a major influence on the understanding of processes at surfaces relevant to catalysis. Real catalysts are complex materials, and in order to approach an understanding at the atomic level, it is necessary in a first step to drastically reduce complexity and then systematically increase it again in order to capture the various structural and electronic factors important for the function of the real catalytic material. The use of thin oxide films as templates to mimic three-dimensional supports as such or for metal particles as well as to model charge barriers turns out to be appropriate to approach an understanding of metal–support interactions. Thin oxide films also exhibit properties in their own right that turn out to be relevant in catalysis. Thin oxide film formation may also be used to create unique two-dimensional materials. The present perspective introduces the subject using case studies and indicates possible routes to further apply this approach successfully.

INTRODUCTION

A detailed understanding of processes at surfaces requires knowledge of the surface structure at the atomic scale. Unraveling this knowledge for metal surfaces was the cause of 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.^{1,2} The surface science approach was limited for quite a while to metal single crystal surfaces. Only in the mid-1990s, the books by Cox,³ by Henrich and Cox,⁴ and by Noguera⁵ on Oxide Surfaces alerted the broader community that this important class of materials should also be included into considerations 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 the TiO₂(110) surface.^{6,7} Henrich and Cox^{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.^{8–17} The idea was to grow oxide films on metal single crystals using the rules of epitaxial growth. They would be made sufficiently thin that surface charging when using charged information carriers, such as electrons or ions, would not occur. The field has further developed tremendously in recent years. Two books^{18,19} and a number of review articles have been published on the subject since,^{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 in Table 1. The present perspective will discuss a number of examples, mainly from the laboratory of the author

Table 1. Experimental Techniques Used To Study Thin Oxide Films^a

technique	acronym
X-ray photoelectron spectroscopy (including ambient pressures)	XPS (AP-XPS)
high resolution electron energy loss spectroscopy	HREELS
photoemission electron microscopy	PEEM
photoemission scanning tunneling microscopy	PHSTM
single crystal microcalorimetry	SCMC
temperature-programmed desorption	TPD
temperature-programmed reaction spectroscopy	TPRS
molecular beam scattering	MBS
photoinduced desorption spectroscopy (including synchrotron, laser (+ ultrafast) excitation)	PIC
low energy electron diffraction	LEED
low energy electron microscopy	LEEM
scanning tunneling microscopy	STM
atomic force microscopy	AFM
electron spin resonance (including high-field ESR)	ESR
infrared reflection absorption spectroscopy (including polarization modulation)	IRAS
sum frequency generation	SFG
second harmonic generation	SHG

^aFor a review of some techniques, see ref 167.

Table 2. Systems Studied

oxide	support
Al ₂ O ₃ (111)	NiAl(110)
CaO(100)	Mo(100)
CeO ₂ (111)	Ru(0001)
Cr ₂ O ₃ (111)	Cr(0001)
Fe ₂ O ₃ (111)	Pt(111)
Fe ₃ O ₄ (111)	Pt(111)
Fe ₃ O ₄ (111)	Ag(111)
MgO(100)	Mo(100)
MgO(100)	Ag(100)
RuO ₂ (110)	Ru(0001)
SiO ₂ bilayer	Ru(0001)
SiO ₂ bilayer	Pt(111)
ZnO(0001)	Pt(111)
ZnO(0001)	Ag(111)

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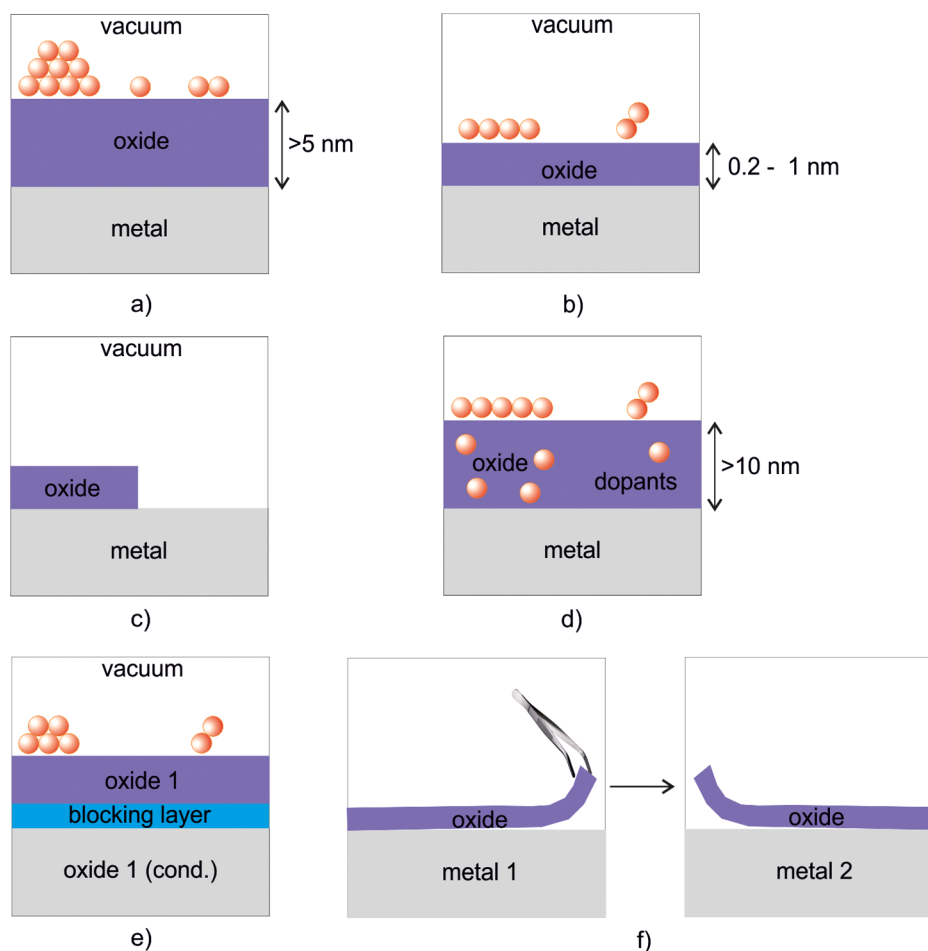


Figure 1. Schematic illustration of various thin film systems and scenarios.

(Table 2 contains the systems at which the group of the authors have primarily looked), in order to demonstrate how the field has developed and where are interesting avenues for future research in this area.

Before we discuss specific examples, I would like to address a few general scenarios, as schematically indicated in Figure 1. Figure 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 properties of the oxide film surface. 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 Figure 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.¹⁹ Examples are silica films,^{20–22} aluminosilicate films,²³ modeling zeolites (see below), or films of quasicrystals.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 release an electron from the buried oxide–metal interface does not exceed the energy gain released by attaching this electron to an adsorbate, then this process is favorable if an appropriate electron

transport mechanism is available in the system under consideration.^{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 that 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 (Figure 1c).²⁸

Some researchers call this an inverse catalyst (inverse with respect to metal particles on oxides) that allows the interrogation of the oxide–metal interface via comparison.^{29–31}

The use of such nomenclature is somewhat misleading, because 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 interface will be different. Still, those investigations may be useful in their own right. A situation, schematically represented in Figure 1c, may be encountered when dealing with the so-called strong metal support interaction (SMSI).^{32–41} The scenarios sketched in Figure 1b,c are, of course, relevant to model catalysts and conceptual of such studies also offer the possibility to combine them with approaches modeling the bulk situation based on the scheme depicted in Figure 1a. Figure 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.^{42–48} If the appropriate combination between host material and

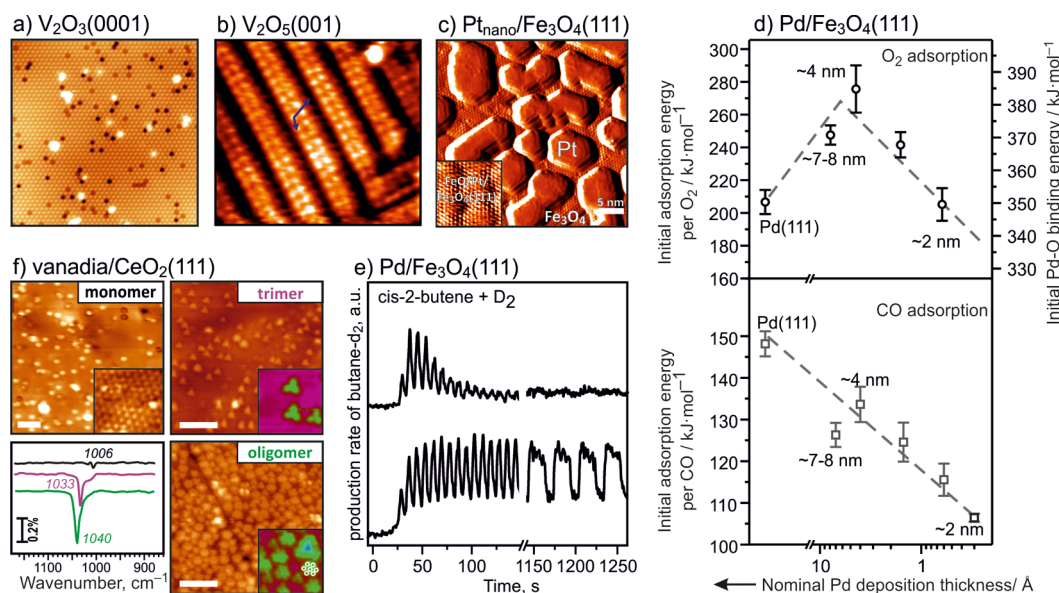


Figure 2. Case studies on thin film systems simulating the oxide bulk situation. (a) STM image of the $\text{V}_2\text{O}_3(0001)$ surface. Reprinted with permission from ref 61 (<http://dx.doi.org/10.1103/PhysRevLett.114.216101>). Copyright 2015 American Physical Society. (b) STM image of the $\text{V}_2\text{O}_5(001)$ surface. Reproduced from ref 66. Copyright 2008 American Chemical Society. (c) STM image of Pt nanoparticles on $\text{Fe}_3\text{O}_4(111)$. Here the system had been heated, so that the Pt nanoparticles are covered with an ultrathin FeO layer (see inset). (d) Single crystal calorimetry data on $\text{Fe}_3\text{O}_4(111)$ supported Pd nanoparticles as a function of particle diameter for $\text{CO}^{(b)}$ and $\text{O}_2^{(a)}$ adsorption. Reproduced with permission from ref 73. Copyright 2013 John Wiley & Sons, Inc. (e) Molecular beam experiments for *cis*-butene hydrogenation on $\text{Pd}/\text{Fe}_3\text{O}_4(111)$ at 260 K. The mass spectrometry signal of butane has been recorded for clean Pd particles (left) and after decoration with carbonaceous species (right). Reproduced with permission from ref 84. Copyright 2008 John Wiley & Sons, Inc. (f) STM images of vanadia clusters formed on $\text{CeO}_2(111)$. The inset shows atomic resolution of the vanadia particles. The infrared spectra (left, bottom) show the shift of the vanadyl band as a function of vanadia particle size. Reproduced with permission from ref 92. Copyright 2009 John Wiley & Sons, Inc.

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 ultrathin 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.^{49,50} Realizing that dopants control the electronic properties of oxides offers yet another possibility for studying ultrathin films. Imagine the situation depicted in Figure 1e: Here, an ultrathin oxide film is grown homoepitaxially on a specially prepared substrate of the same oxide.^{51–53} In this substrate, oxide oxygen vacancies have been created by reduction, which renders the substrate conductive. Given the envisioned homoepitaxial 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 were 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 that needs to be included conceptually in this introduction. This aspect is concerned with the possibility to remove ultrathin films from their substrate to create true two-dimensional materials (Figure 1f), similar to graphene,^{54–56} but based on oxides.^{57,58} Those films may, of course, be used to create stacks of two-dimensional materials of varying stoichiometry and varying electronic properties.⁵⁹

EXAMPLES

Representation of Bulk Oxide Materials and Supported Nanoparticles. We start with an example for a film representing the bulk material (referring to Figure 1a, that is, vanadium-sesquioxide ($\text{V}_2\text{O}_3(0001)$, Figure 2a).^{60–63} There has been a long debate on the surface termination of this oxide, which is a relevant material in catalysis, because vanadium-oxides are used as oxidation catalysts in important reactions such as the oxidation of SO_2 to SO_3 in the production of sulfuric acid. Originally it had been proposed that $\text{V}_2\text{O}_3(0001)$ (Figure 2a) is terminated by vanadyl groups, that is, V–O double bonds, as evidenced through characteristic vibrational features.^{64,65} However, a quantitative photoelectron diffraction study came to the conclusion that the surface is terminated by an oxygen layer with vanadium ions rearranging underneath that layer in order to compensate for the polarity of the surface.⁶⁰ Recently, a detailed study of surface preparation using the thin film approach has been performed, and it has not been possible to reproduce this surface termination. Instead, a combined LEED I/V and STM study has been undertaken, which unambiguously provides evidence for a vanadyl-terminated surface,^{61–63} which corroborates previous studies and settles the structure determination. Here, it was the careful preparation that proved essential. Similar studies have been performed for vanadium-pentoxide surfaces ($\text{V}_2\text{O}_5(001)$) (Figure 2b), which is actually an insulating material and hard to study as bulk material.^{66,67} The film was grown on a $\text{Au}(111)$ surface and showed the perfect structure expected for this layered material from the bulk structure. As pointed out, knowing the structure at the atomic level is important. However, if ensemble-averaging techniques are applied, knowledge at the mesoscopic scale is of equal importance. To cover

this area, Schmidt and collaborators carried out LEEM/PEEM studies of oxide films. Iron oxide films and their thermal transformations have been studied in detail, for example, refs 68 and 69. Those surfaces may then be investigated with respect to adsorption of a variety of molecules and the deposition of nanoparticles and are considerably stable against desorption of molecules and thermal treatment. To exemplify the studies on nanoparticles, I refer to a series of studies on Pd and Pt nanoparticles on a thick magnetite $\text{Fe}_3\text{O}_4(111)$ film (Figure 2c).^{33,70,71} For some of those systems, we studied the adsorption of CO as a function of particle size in the range from particles containing several thousand atoms to particles containing only 100 atoms.^{72–75} We applied the technique of single crystal microcalorimetry (SCMC) as developed by Campbell and co-workers⁷⁶ in this case for the first time to study adsorption on deposited nanoparticles. Such studies are only conceivable using the thin film approach. It is found that while particles of a few thousand atoms, exposing mainly Pd(111) facets, approach the value observed for Pd(111), the heat of adsorption is still considerably smaller and systematically decreases, as predicted theoretically by the Röscher group,^{77–79} to a value close to half of the value for the single crystal^{80–82} upon reaching a few hundred atoms (Figure 2d). This was corroborated by a later study.⁸³ Those results are clear indications that the use of slab calculations to describe molecular adsorption on disperse metal catalysts even with relatively large particles, probably, is not the last word. With respect to chemical reactions, we investigated hydrogenation of butene and selective hydrogenation of acrolein on Pd and demonstrated by molecular beam experiments (Figure 2e) that hydrogenation is triggered by a complex interplay between adsorbates forming in an induction period, in particular for selective hydrogenation, and delivery of hydrogen to the surface.^{84–88} Hydrogenation is decisively influenced by carbon deposited on the edges and corners of the particles in the early stages of the reaction, which controls the diffusion of hydrogen between the surface, where the reaction takes place, and the interior of the particle.^{84–86,89} For this to be effective, the hydrogen has to reside close to the surface, which is the natural situation in a nanoparticle but is not found for a single crystal, where hydrogen diffusion into the subsurface region is suppressed and if it would migrate hydrogen would diffuse away from the surface and dissolve in the bulk. The application of resonant-nuclear reaction analysis⁹⁰ to determine the hydrogen subsurface against surface hydrogen was decisive. This demonstrates that studies on Pd single crystals would not allow a conclusive evaluation of the reaction mechanism. Not only metal nanoparticles, but oxide particles as well may be prepared on an oxide thin film substrate. Based on previous experience by Mullins et al.,⁹¹ it is possible to grow well ordered ceria ($\text{CeO}_2(111)$) films on top of a Ru(0001) surface. By evaporation of vanadium in an oxygen ambient atmosphere, vanadia particles of increasing sizes may be prepared and studied with respect to their reactivity.^{92,93} We have investigated the oxidation of methanol to formaldehyde as a function of vanadia particle size. The systems may be well characterized via STM and IR as well as photoelectron spectroscopy, and the redox mechanism of electron transfer between vanadia particles and ceria may be unambiguously identified (Figure 2f). While the pure ceria films do oxidize methanol to formaldehyde at 600 K, the small vanadia particles perform the reaction at slightly above room temperature. Sauer and his group^{92,94} have been able to elucidate via density

functional calculations the mechanism at an atomic level and show that a vanadia trimer, identified via STM (Figure 2f), leads to the observed thermal reaction spectra. Quantitative agreement between the observations and the theoretical calculations may be achieved. Another interesting application of thin film techniques to determine properties of surfaces of bulk materials is connected with the use of electron paramagnetic resonance (EPR) spectroscopy to study the properties of color centers in MgO.⁹⁵ Oxide single crystals typically contain a number of defects, including oxygen vacancies, that is, potential color centers, which would swamp any signal characteristic for the surface. However, if thin MgO films are grown on a metal such as Ag or Mo, the surface is dominant, and using an ultrahigh-vacuum EPR setup, the surface EPR signals may be recorded and identified through quenching experiments using oxygen from the gas-phase as demonstrated by Risse and collaborators.^{96–101} Sterrer et al. have taken this a step further by bringing those films into an ambient atmosphere to attempt to add to those studies another step, including models for wet impregnation of oxides.^{102–106}

Systems Modeling Charge Transfer to Adsorbates.

The next example refers to the use of ultrathin films to study electron transfer (see Figure 1b). Here, also MgO films are considered (Figure 3a). Parkins et al.¹⁰⁷ had demonstrated that MgO films can be used as tunneling barriers for magnetic storage devices. Pacchioni and co-workers²⁵ in a series of papers used the idea of a MgO tunneling barrier to predict the influence of electrons tunneling through a film on the morphology of Au nanoparticles. While Au_{20} remains in its three-dimensional tetrahedral structure¹⁰⁸ on a bulk MgO(100) surface, the deposition of the same particle onto a thin, two layer thick film assumes a flat, raft-like morphology due to electrons tunneling to the Au particle, which in turn assumes a morphology that warrants the closest contact of the constituting, electronegative Au atoms to the oxide in order to accumulate the electronic charge. This prediction has been verified experimentally by Sterrer et al.²⁷ using STM by comparing MgO films of thicknesses of three and eight monolayers with respect to Au deposition. While eight layers already behave similar to bulk MgO, where Au adopts a three-dimensional morphology, three MgO layers support the formation of two-dimensional Au nanoparticles. One reason for the different behavior is the softness of the MgO phonons when MgO films are ultrathin, as proven experimentally by Rocca et al. using HREELS.¹⁰⁹ The coupling between phonons and electron transfer leads to a polaronic distortion of the substrate, which stabilizes the charge on the Au particles. These flat Au particles have been studied in detail with respect to their electronic structure in relation to their morphology and structure. In particular, the opening of the gap between occupied and unoccupied states has been investigated as a function of various parameters, that is, number of atoms in the particles, average number of nearest neighbors, and shape.¹¹⁰ There is no unique extrapolation of the gap closing possible as a function of the number of atoms. It depends on all three parameters simultaneously. Niluis et al.¹¹⁰ proposed to use a parameter, the so-called linear eccentricity, which relates the size to the shape, to extrapolate the gap closing. Häkkinen and collaborators^{111–114} have studied these systems on the basis of theoretical models and have suggested that there is substantial electron transfer to the particles, amounting to about 0.2 electrons per atom. Those predictions were also tested for smaller Au rafts.¹¹⁵ Here, STS has been used to determine the

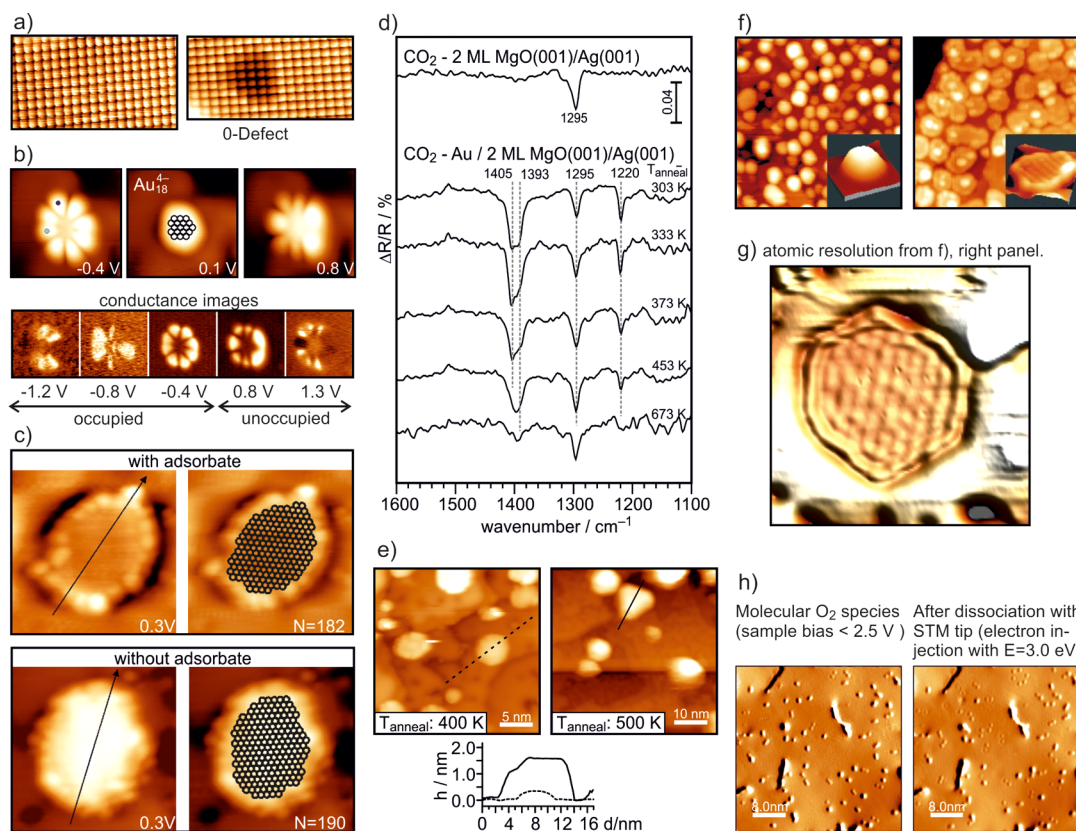


Figure 3. Case studies on thin film systems used to study charge transfer through an oxide film onto a supported metal particle or a molecular adsorbate. (a) STM image of the MgO(100) film (left) without defect and (right) with an oxygen vacancy. Reproduced with permission from ref 18. Copyright 2011 John Wiley & Sons, Inc. (b) $\text{Au}_{18}^{+}/\text{MgO}(100)$ STM images as a function of tunneling voltage (lower panels). Conductance images for the voltages indicated. Reprinted with permission from ref 115 (<http://dx.doi.org/10.1103/PhysRevLett.102.206801>). Copyright 2009 American Physical Society. (c) STM images of Au islands on MgO(100) after (left) and before (right) exposure to CO_2 . Reproduced with permission from ref 119. Copyright 2015 John Wiley & Sons, Inc. (d) IR spectra for MgO(100) (top) and Au/MgO(100) (below) after exposure to CO_2 as a function of preheating the system. Reproduced from ref 88 with permission from the Royal Society of Chemistry. (e) STM images of Au/MgO(100) islands after preheating to 400 and 500 K, respectively. Reprinted with permission from ref 88. Copyright 2015 American Physical Society. (f) STM images of Au islands on thick CaO(100) layers without (left) and with Mo^{+} doping. Higher resolution images of an individual particle in the insets. Reproduced with permission from ref 47. Copyright 2011 John Wiley & Sons, Inc. (g) STM images with atomic resolution of a Au island on Mo-doped CaO(100). Reproduced with permission from ref 110. Copyright 2015 John Wiley & Sons, Inc. (h) STM images of oxygen molecules on Mo-doped CaO(100) before (left) and after (right) oxygen dissociation. Reproduced with permission from ref 43. Copyright 2013 John Wiley & Sons, Inc.

symmetry of occupied and unoccupied levels and count the number of electrons on the particle, similar to the originally report for another system, small Au chains on thin alumina films, the groups of Sauer and the author.¹¹⁶ A flat Au_{18} (Figure 3b) almost circular raft has been determined to carry four electrons, whose interaction is kept minimal via the nodal planes induced by the symmetry of the raft. When the rafts get larger, the extra electrons have a tendency to localize at the rim of the particle in order to minimize repulsion, which was predicted by Häkkinen and his group and verified by Lin et al.¹¹⁷ This led to the idea that molecules might reside at the rim. If one would be able to image them, this would provide a model to further study the interplay between charges on metal particles and the metal-particle–oxide interface. Three systems have been investigated to study the electronic effects of molecules at the rim, both on the molecules themselves and in the Au particle. In an early study, inelastic electron tunneling spectroscopy on the low lying frustrated rotations of CO (45 meV excitation energy) has been used to image CO molecules on the rim of an arbitrarily shaped Au raft.¹¹⁷ However, direct imaging of the position of individual molecules was not

possible. Stiehler et al. succeeded in imaging isophorone molecules, which only interact weakly with the Au particle, at the rim and, in fact, were able to study the identical Au particle with and without molecules adsorbed by using the tunneling tip to manipulate the molecules at the rim.¹¹⁸ This study allowed them to investigate the influence of physisorbed molecules on the electronic structure of quantum well states developing in those finite Au rafts due to the finite size of the system. It was shown¹¹⁸ that the molecules act on the Au states by providing additional room to delocalize the Au electrons and weaken the barrier for confinement of the quantum well states, thus increasing the energy separation of states and lowering the effective mass of the Au electrons. If the Au particles were exposed to carbon dioxide, an interesting chemistry was observed. Spontaneously, oxalate, $\text{C}_2\text{O}_4^{2-}$, a CO_2 dimer held together by a C–C bond, is formed (Figure 3c).^{88,119} What looked surprising at first glance may actually be expected upon closer inspection. Transferring an electron to individual CO_2 molecules affords 0.6 eV and is accompanied by substantial activation energy, necessary to bend the molecule^{120–123} (according to the Walsh diagram,¹²⁴ we proceed from a linear

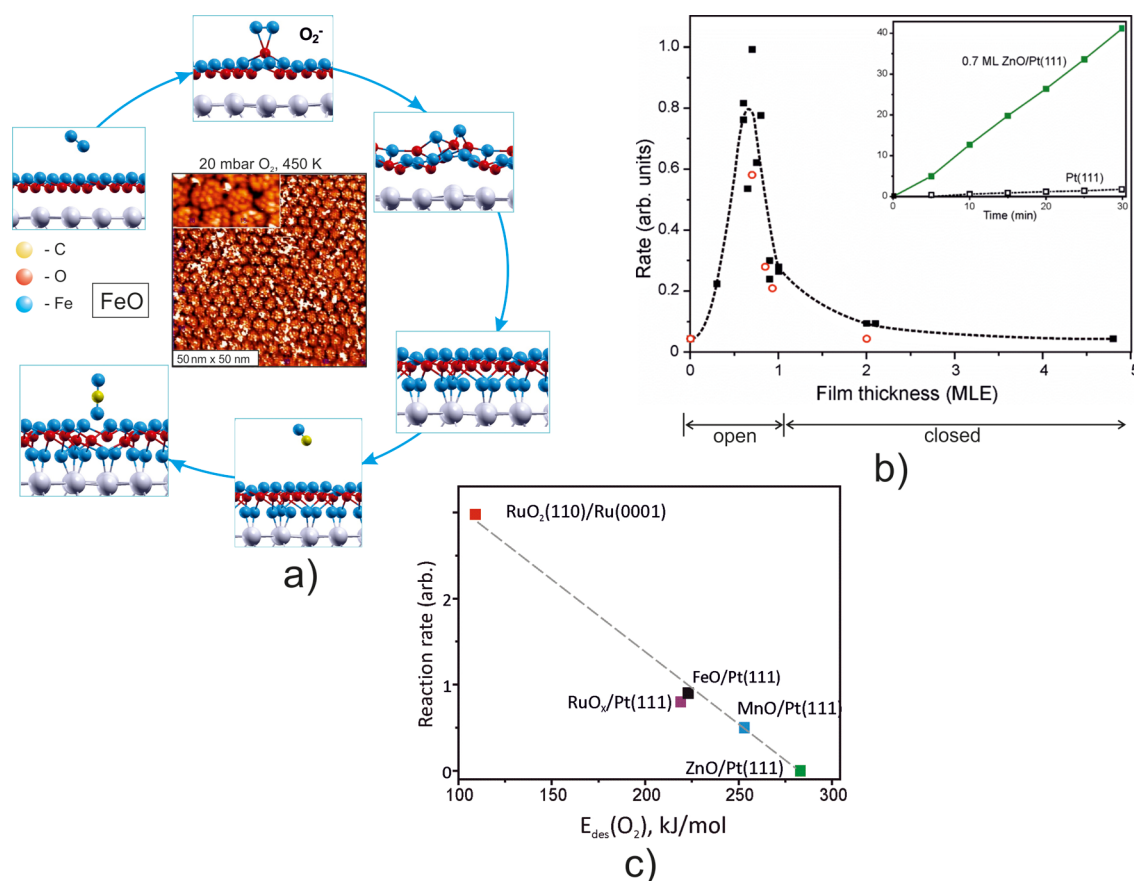


Figure 4. Case studies on the reactivity of ultrathin films with and without full metal coverage. (a) STM images of a FeO layer on Pt(111) after exposure to 20 mbar of O₂. The inset shows details of the structure. DFT calculations reveal the catalytic cycle of how the FeO film transforms and catalyzes CO oxidation. Reproduced with permission from ref 39. Copyright 2010 John Wiley & Sons, Inc. (b) Reactivity measurements for CO oxidation of ZnO/Pt(111) as a function of ZnO coverage. The region where the layer covers the surface fully is indicated. Reprinted from ref 28, Copyright 2013, with permission from Elsevier. (c) Comparison of CO oxidation reaction rate as a function of oxygen desorption energy from the thin film system, when the oxide covers the metal support completely. Reproduced with permission from ref 140. Copyright 2013 John Wiley & Sons, Inc.

16 electron system to a bent 17-electron system as from CO₂ to NO₂). However, as was shown decades ago by molecular beam experiments in the gas phase by Märk, Herschbach, and others^{125–128} and supported by theory, transferring an electron to a CO₂ dimer is favored by 0.9 eV. Once the dimer ion has been formed, one may imagine that the high density of electrons on the Au particles provides sufficient driving force to transfer a second electron and favor the formation of a C–C bond and the oxalate ion, bound to the metal particle, consecutively. Indeed, the oxalate was identified through IR spectra including conclusive isotopic labeling of the used CO₂ as ¹³CO₂ and C¹⁸O₂, as well as of the MgO film as Mg¹⁸O (Figure 3d).^{88,119} We note at this point that it is one of the advantages of the thin film preparation technique to be able to easily isotopically label the substrate as well as the adsorbate, which allows checking the involvement of substrate oxygen in chemical processes at the surfaces. The presence of the oxalate ions at the rim has clear consequences for the quantum well states of the Au rafts: The electrons in the Au rafts are repelled by the localized electrons on the oxalate ions and, consequently, feel an increased barrier at the rim, leading to a larger energy spacing of the quantum well states, compared with the those on the raft without molecules and, thus, to an decrease of the effective mass of the Au electrons.¹¹⁸ From a reactivity point of view, it is interesting to look again at the prediction that

Pacchioni and collaborators made:²⁵ while the formation of the flat Au rafts was accompanied or even caused by transfer of electrons, particles that are three-dimensional would not show any electron transfer. Therefore, if it were possible to create three-dimensional particles from the rafts, for example, by increasing the temperature before exposure to CO₂, the formation of oxalate, caused by the transferred electrons, would have to be suppressed. This, indeed, is observed, thus corroborating the predictions fully (Figure 3e).¹¹⁰ The reactivity of this system may now be explored further by studying interaction with other molecules, such as, H₂, H₂O, and NH₃. Studies in those directions are under way.

Doping for Controlling Charge Transfer. The concept of using a tunneling barrier to transfer electrons to a metal particle, thus forcing it to adopt its morphology, which in turn controls the particles chemistry, would be of interest for catalysis, if it could be transferred to a realistic system not based on an ultrathin film but rather on a bulk material. This brings us to an example in line with the comments on Figure 1d. Here, the proposal has been to use dopants in a thicker film, instead of the metal support below the ultrathin film, as a source of electrons to stimulate similar phenomena in bulk materials. This has been realized for thick CaO films grown on a Mo(100) substrate. Here, upon heating Mo may diffuse into the CaO film and replace Ca ions from their positions so as to

dope the crystal, or one may first grow a thinner CaO film, add the dopant from the vapor, and cover the doped material with more CaO layers.^{42,44,129,130} Typical dopant levels are on the order of 1–2%. The consequences for Au nanoparticles are quite substantial when doped and undoped materials are compared.⁴⁷ While for the undoped CaO film the Au particles exhibit three-dimensional shape as revealed by STM, the Au particles on the doped material are two-dimensional. STM reveals even the Moiré structure of the one-layer Au rafts caused by the interference between the Au lattice and the CaO lattice underneath (Figure 3f,g). Calculations by the Pacchioni group show that the mechanism is very similar to the one discussed above for the ultrathin film system.⁴⁷ It is the nature of the dopant and the ease of allowing the removal of electrons that determines whether charging of the Au and formation of the rafts may occur. Studies on the tunneling process in such doped materials indicate a mechanism of electron hopping based on coupling to a surface phonon-polariton in the oxide material. Having been able to demonstrate that the concept developed above also holds for bulk materials, it is possible to follow the ideas perhaps on real catalytic material. Work in this direction is in progress. Again, it is the combination of dopants and host material, as well as choosing the appropriate adsorbate, that determines the outcome. Häkkinen and his group have undertaken a study to look into various dopants and to find the optimal material.¹³¹ Experimentally, we have undertaken a study of molecular oxygen adsorption on doped CaO in collaboration with the group of Joachim Sauer, in order to evaluate the applicability of the concept to other areas.⁴³ Here, the question was related to the activation of oxygen in connection with oxidative methane coupling. We were able to show through a combination of experiment and theory, that dioxygen binds to the dopant positions, even when they are considerably below the surface, and concomitantly electrons are transferred to produce a superoxo species with an elongated O–O bond (Figure 3h). This represents yet another example for the validity of the concept developed above. In this case, Schlögl's group¹³² has undertaken initial studies on powder materials.

Strong Metal–Support Interaction and Open Oxide Film–Metal Interfaces. Another example, for studies using ultrathin films, is connected with the so-called strong metal–support interaction, where oxide from the support migrates onto a metal particle. This oxide film may be completely different in structure and stoichiometry compared with the supporting oxide. In fact, the structure and stoichiometry may change since the chemical potential during the reaction is set by the pressure and composition of the gas phase (Figure 4a).^{14,71,133} In this case, a situation is created that might be depicted as shown in Figure 1b,c. There is either a closed film covering the particle or an open metal–oxide interface (Figure 4b). The chemical constitution of fully closed/covering films (Figure 4c) may vary along with their chemical reactivity, and the latter may undergo even more pronounced alterations as we open the oxide–metal interface. SMSI states are often less reactive than the clean metal particles, but there is also the situation where the reverse is true. Shaikhutdinov et al.^{38,67,133} have reviewed this in detail in a number of papers, and we will not repeat this here. Still there are a number of controversies with respect to the question of how iron oxide ultrathin films overgrowing Pt and Pd nanoparticles influence reactivity.^{134–136} Also, ZnO films are actively investigated.^{137,138} Despite preparation in pure oxygen ambient atmosphere, the “as

grown” ZnO films on Pt(111) expose hydroxyl groups. In contrast, a bilayer film on Ag(111) does not exhibit OH species, not even upon dosing of hydrogen or water. The results show that hydrogen may efficiently be provided by a Pt support, even for the multilayer films, via hydrogen dissociation and subsequent diffusion of H atoms through the film.¹³⁹ Future studies will hopefully resolve those controversies.

Homoepitaxial Oxide Films on Conducting Oxide Supports. Before we come to the last example, we would like to address the homoepitaxial growth of a thin TiO₂ film on a TiO₂ single crystal, which has been made conductive via heating *in vacuo*, thus creating a support that allows STM to be performed.⁶ Titania thin films grown on metal supports usually show islanding, and it is difficult to prepare films fully covering the metal surface.¹⁴¹ Therefore, it is desirable to look for suitable substrates for growth. Such a substrate is the above-mentioned rutile/TiO₂(110) single crystal that has been made conductive and appears dark blue or black. In regular studies on single crystal TiO₂, such conductive samples are used as well. However, because surface chemistry may be influenced by doping in the bulk⁴³ as demonstrated above, one would like to be able to study a material with little bulk defects in an attempt to unravel its influence. This may be achieved by homoepitaxially growing TiO₂ films of varying thickness on a conductive TiO₂(110) single crystal. Kühlenbeck and co-workers⁵¹ have recently studied such systems and found that the diffusion of the oxygen vacancies, needed for conductivity, may be suppressed toward the homoepitaxially grown film by a blocking layer grown on top of the TiO₂ crystal by evaporation of small amounts of Ta (Figure 5). This blocking layer

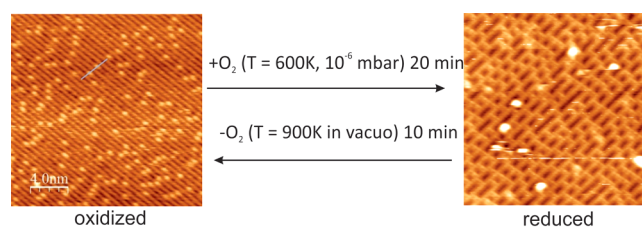


Figure 5. Homoepitaxially grown TiO₂ film on a conducting TiO₂(110) single crystal covered with a (Ti + Ta₂O₅) blocking layer. Reprinted with permission from ref 51. Copyright 2016 American Chemical Society.

effectively suppresses diffusion and allows one to quickly manipulate the film grown on top. This approach needs to be explored more in the future, but it holds potential.

Silica Films. The last example is concerned with silica. Silica is an important support for a number of catalytic systems. One prominent example is the Philips catalyst for ethene polymerization.¹⁴² Often, those supports are amorphous and contain hydroxyl groups, which represent anchoring sites for metal atoms, such as Cr in the case of the Philips catalyst. However, in order to fulfill the requirement stated in the beginning of this perspective, we would need to understand the local structure of the silica. My research group started to work on this problem 15 years ago,^{143,144} and we are close to reaching the final goal. In the following, I will summarize the present status and point to our future work in this area. After we had succeeded to prepare the first monolayer silica film on Mo(112) in 2005,¹⁴⁵ which not yet had the correct stoichiometry, it took another 5 years to prepare a bilayer silica film with proper SiO₂ stoichiometry on Ru(0001).²⁰ Those silica films are composed

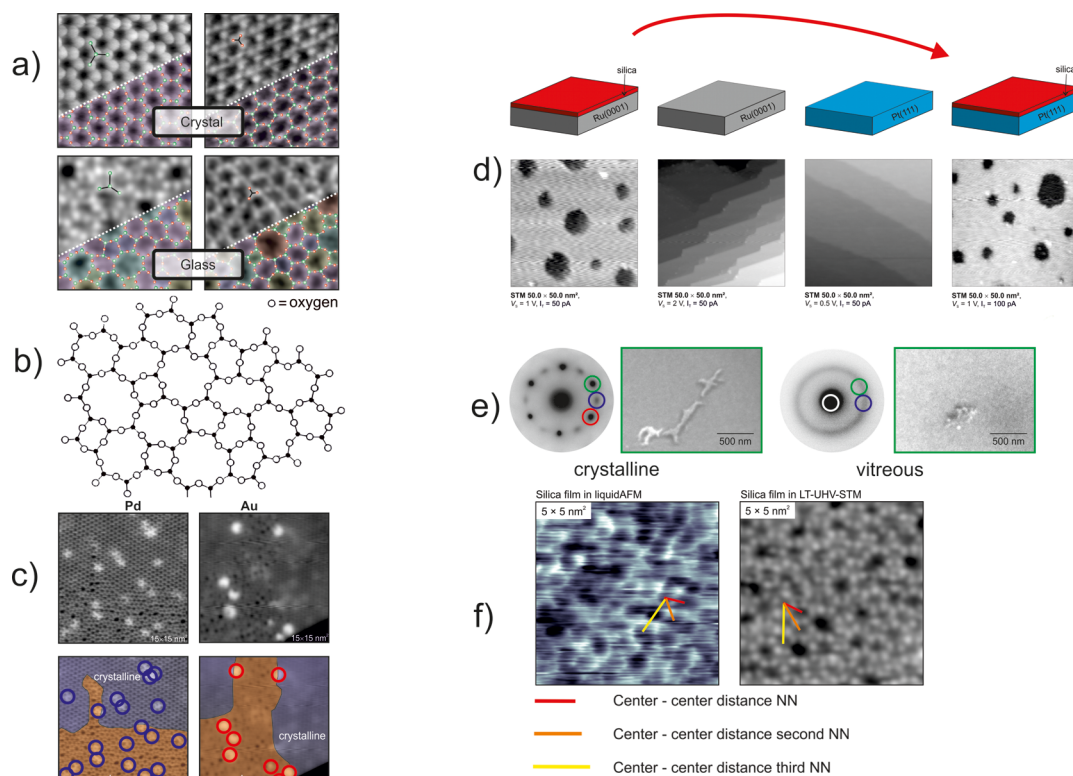


Figure 6. Case studies on a bilayer SiO_2 film. (a) STM images with atomic resolution of a SiO_2 bilayer film showing the positions of Si atoms at the (left) and O atoms at the (right). The images at the top are areas with crystalline and vitreous or glassy structures at the bottom. Reprinted with permission from ref 21. Copyright 2012 American Chemical Society. (b) Schematic representation of a silica glass structure proposed by W. H. Zachariasen in 1932. Reprinted (adapted) with permission from ref 149. Copyright 1932 American Chemical Society. (c) STM images of an area of the SiO_2 bilayer film showing coexisting crystalline and vitreous structures after deposition of Pd (left) and Au (right) atoms. The smaller Pd atom can be identified on both structures, while Au prefers vitreous areas exposing pores with ring sizes larger than six. Reprinted with permission from ref 153. Copyright 2014 American Chemical Society. (d) Experimental evidence through STM imaging (the black areas are characteristic holes in the film) of a successful transfer of a vitreous silica bilayer from Ru(0001) to Pt(111) support via a polymer assisted lifting procedure.⁵⁷ (e) LEED (left) and STM (right) images of the crystalline and vitreous bilayer silica film. Reprinted from ref 163, Copyright 2016, with permission from Elsevier. (f) AFM image of the bilayer SiO_2 film under a water droplet (left, at near atomic resolution), indicating the high stability of the film. STM image in vacuum (right, atomic resolution) for comparison. Reprinted from ref 164 with the permission of AIP Publishing.

of corner sharing SiO_4 tetrahedra forming a hexagonal, honeycomb arrangement. In the monolayer, one of the four Si–O bonds is bound directly to the metal giving rise to a stoichiometry of $\text{SiO}_{2.5}$ with strong silica–metal interaction. In the bilayer, two such monolayers are connected via a common Si–O–Si bond, which leads to the proper stoichiometry of SiO_2 for the film. The film is an excellent insulator with a wide band gap.^{146,147} The latter bilayer is only weakly bound to the metal, basically via a van-der-Waals interaction. Interestingly, this bilayer comes in a crystalline form described above or in an amorphous or vitreous form (Figure 6a),¹⁴⁸ where the layer does not exhibit, exclusively, six-membered honeycombs but an arbitrary arrangement of various ring sizes ranging from four- to nine-membered rings, whose occurrence follows a log-normal distribution. Heyde et al.^{21,22} have imaged both the crystalline and the amorphous film at atomic resolution. In fact, this has allowed us to verify the so far only indirectly proven model for a glass proposed by Zachariasen and published in 1932 in *JACS* (Figure 6b).^{21,22,149} The vitreous film has also been prepared on Pt(111)¹⁵⁰ and on Pd(100).¹⁵¹ This film is the desired support to which metal atoms should be anchored. In order to do so, the film needs to be hydroxylated, which turned out to be difficult and only possible through electron bombardment of a water layer condensed onto the film.¹⁵² The created hydroxyls

have been characterized by IR spectroscopy. At present Cr is being deposited in order to transform the structural model into a model catalyst. Without hydroxylation, it has been possible to deposit metal atoms (such as Au and Pd) and image them, but there is a tendency to penetrate into the silica openings if the size of the metal allows (Figure 6c).^{153–155} The final steps will then be to study ethene polymerization. There are further research directions that are directly related to the silica films. One is the substitution of Si atoms by Al atoms in an attempt to prepare aluminosilicates²³ or models for a zeolite with infinite pore-size. The other one is to remove the van-der-Waals bound silica bilayer from the metal substrate⁵⁷ and use it to produce composite stacks of two-dimensional materials involving other 2D materials such as graphene or other 2D oxides or 2D sulfides. The first goal has been reached, and an aluminosilicate film has been prepared and characterized in collaboration with Joachim Sauer's group.²³ Based on IR frequency shifts of probe molecules such as CO and ethene those 2D-zeolite films are very acidic; in fact, they appear to be more acidic than a 3D zeolitic material called chabazite. The chemistry of such material will be studied in the future, and the further substitution of Si by other elements (C, Fe, Ti) and the consequences for the observed chemistry will be investigated.^{156–158} Very recently, a step forward to the second

goal has been reached. In recent work, Büchner et al.⁵⁷ succeeded to peel off the silica film from a Ru(0001) substrate, deposit it onto a Pt(111) substrate, and record STM images proving that the transfer had been successful (Figure 6d). This could be the starting point for future research creating 3D structures. Another comment on the use of the silica film: Due to its weak bonding to the substrate, small molecules may diffuse underneath the film, as has been proven for CO, oxygen, and hydrogen.^{159,160} This could give rise to reactions underneath the silica film and would allow us to study chemistry in confined space. Similar attempts have recently been made also for graphene^{161,162} using LEEM. Schmidt and collaborators¹⁶³ have started to investigate the bilayer silica film using LEEM/PEEM (Figure 6e). Recently, also, the bilayer silica film has been studied under water using AFM at close to atomic resolution (Figure 6f).¹⁶⁴ This film may represent a promising substrate to study wet impregnation of silica as used in catalyst preparation.

■ SYNOPSIS

Studies such as those described in this perspective could be useful to get closer to a full understanding at the atomic level of processes at heterogeneous catalysts by catching some or perhaps even all of the relevant complexity of the real material. However, there is much more to gain: it seems possible to develop concepts that allow one to even design materials and to transfer the knowledge from the model system to the real catalytic system in an attempt to design new systems. Besides this, fundamental aspects, going beyond catalysis, may be investigated, as exemplified by the study of amorphous oxides. Having full atomic control of the material always opens avenues for further more exciting research. Imagine if we succeeded to prepare well-structured sulfide films. Those may be interesting in their own right, but they would also be interesting in comparison to the corresponding oxides. One should not forget that sulfides, not oxides, are considered as important substrates in fundamental questions concerning the origin of life.^{165,166}

■ AUTHOR INFORMATION

Corresponding Author

*freund@fhi-berlin.mpg.de

Notes

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