

# Ultrathin oxide films on metal supports: Structure-reactivity relations

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## Acronyms

UHV – Ultra-High Vacuum  
STM – Scanning Tunneling Microscopy  
XPS – X-ray Photoelectron Spectroscopy  
TPD/TPR – Temperature Programmed Desorption/Reaction  
LEED – Low Energy Electron Diffraction  
SXR – Surface X-ray Diffraction  
AES – Auger Electron Spectroscopy  
LEEM – Low Energy Electron Microscopy  
DFT – Density Functional Theory  
EPR – Electron Paramagnetic Resonance  
M-vK – Mars-van Krevelen (mechanism)

## Keywords

Heterogeneous Catalysis  
Ultrathin Oxide Layers  
Model Systems  
Surface Structure

## Summary points

1. Ultrathin oxide films may be grown on metal supports, both from the same or a different metal representing the support.
2. Ultrathin films are flexible with respect to their structure and respond to external stimuli including the chemical potential of the gas phase they are exposed to.
3. Due to the combination of geometric structures and the concomitant electronic structures thin oxide films may be used to control charge transfer from the metal support to adsorbed species and thus trigger chemical reactions.

4. Combinations of surface analytical techniques allow the direct investigation of structure-reactivity relations for ultrathin oxide films and to identify the in-situ formed active phase.
5. The processes involved in active phase formation may be described following ideas put forward in early theories of the oxidation of metals.

### **Abstract**

Well-ordered, thin oxide films have drawn some attention in recent years as suitable oxide supports for modeling highly dispersed metal catalysts at the atomic scale. It turned out, however, that ultrathin oxide films by their own may exhibit interesting catalytic properties. In this review, we discuss phenomena specifically connected to ultra-thin oxide films in order to explain and understand the physicochemical basis of their reactivity in oxidation reactions. Two sets of systems are discussed, i.e. (i) transition metal oxide films grown on metal substrates, and (ii) “native” oxide films formed upon oxidation of metal surfaces.

### **Introduction**

Well-ordered, thin oxide films have drawn some attention in recent years as a way to study dispersed metal catalysts at the atomic scale [1-3]. Their study has contributed considerably to our understanding of such systems, as they allow us to reduce the complexity of the real system, and yet capture – in contrast to metal single crystals – an important part of it, in particular the finite size, and thus the flexibility of the system, and the metal/oxide interface. The latter aspects turn out to be decisive, not always, but in many cases, for a detailed understanding of nano-scaled systems as they are represented by dispersed metal catalysts. When prepared in ultrahigh vacuum (UHV) and under reproducible conditions much may be learned about their thermodynamic stability [4] and concomitantly about adsorption and reaction on those systems, both with respect to the relation between geometric and electronic structures as well as reaction kinetics [5,6]. The relation of the information gained to results of catalytic studies under ambient conditions needs to be carefully evaluated on a case-to-case basis. One important aspect is to know whether the system changes considerably under the applied reaction conditions. As an example consider oxidation reactions where the system is exposed to higher doses or pressure of oxygen together with considerable changes in temperature. As a consequence the supported metal particles may be totally

or partially oxidized, and also the state of the support may undergo substantial changes. Such changes have recently been documented and they have led to the investigation of ultra-thin oxide films from a different perspective [2], which is the exclusive topic of this review. Let us explain what we mean by considering a few examples reported in the literature.

As a first example we consider the so-called Strong Metal-Support Interaction (SMSI) which is known since many years to occur when a dispersed metal catalyst on a reducible oxide support is heated above a threshold temperature in a reducing atmosphere [7-12]. In most cases, the SMSI effect has been assigned to the migration of an oxide layer from the support onto the metal particles, rendering those practically unreactive because the oxide suppresses adsorption of molecules otherwise readily adsorbing on a metal surface. The migrating oxide covers the metal particle as an ultra-thin oxide film whose stoichiometry and structure, again, is often not well known [13-14]. Certainly, the SMSI state depends on the metal, the oxide and the reaction. Nevertheless, it is believed that the encapsulation will deactivate all, and in particular structure-sensitive reactions on metals. But one may raise the question, is this always true? Indeed, the previous statement implies that the encapsulated oxide layer is inert in the reaction and remains unchanged, which is not obvious in the case of ultra-thin films, because their structural and chemical properties are often considerably different from the bulk counterparts [15].

As a second set of examples we address to the recent and still ongoing debates on CO oxidation on platinum group metals (Pt, Pd, ...), in particular on Ru, which was found to be the least reactive under UHV conditions, but the most reactive at technologically relevant (i.e., atmospheric) pressures [16-24]. Here, it was demonstrated, that under reaction conditions the metal surface was covered by an oxidic layer, which originally was thought to represent a dense (1x1) phase of chemisorbed oxygen, and later even a stoichiometric RuO<sub>2</sub>(110) film. Through a controversial interplay between experiment and theory it is now believed that the active phase is neither a chemisorbed oxygen phase nor the stoichiometric RuO<sub>2</sub>(110) phase but rather a very thin ruthenium oxide film of not yet well determined structure.

Of course, oxygen induced restructuring of oxide supported metal nanoparticles may proceed along different routes, which will not necessarily lead to well-defined oxide overlayers but rather ill-defined oxide phases at the metal/support interface [25]. An

example where this has been studied and the spatial confinements of the metal oxide phase in/on the particle to the particle-support interface has been proven is the case of a Pd/Fe<sub>3</sub>O<sub>4</sub>(111) model system [26]. This topic is beyond the scope of the current review and will not be further discussed.

In this review, we will only discuss phenomena specifically connected to ultra-thin oxide films in order to explain and understand the physicochemical basis of their reactivity which can even be traced to some very old ideas discussed in the late forties of the last century.

### **General ideas**

Figure 1 shows a very simple schematic diagram of the situation we are considering. An ultra-thin film is placed onto a metallic substrate. Although, simplified to be structure less in this case, the structure of the ultra-thin film, which is determined by the epitaxial relations to the metal substrate, plays an important role in determining the properties, as will be discussed in the following.

To analyze the situation with the help of simple physical models one has to consider the physical quantities that determine electron transfer, for example, from the metal substrate through the film towards a species located on the film surface. On the one hand, there is the ionization potential that is needed to excite an electron from the metal oxide, which is, in general, not simply the work function of the metal but a related quantity, because it will be substantially modified by the presence of the oxide overlayer. On the other hand, there is the electron affinity of the species adsorbed on the oxide surface to be different from the isolated species, which again may be influenced by the interaction with the oxide surfaces. If the energy balance between those quantities results in an energy gain, then the electron transfer is possible, in principle. However, this is only part of a proper description, because it is not evident how the process would depend on thickness of the film, as the energy balance will only weakly depend on it, and tunneling will be possible, as long as the film is sufficiently thin. Of course, in case of thicker films with a thickness of several nanometers, the tunneling probability, which decays exponentially with thickness, would simply be zero. But why would an oxide film of three layers fundamentally differ from one of, for instance, eight layers with respect to the process? The reason is connected with the degree of lattice flexibility of oxide films, and at this point the structural aspect comes into play. The lattice flexibility is, of course, directly connected with the phonon spectrum of the film, and the latter is altered very

rapidly as the film gets thicker, quickly approaching the phonon behavior of the bulk or a bulk terminating surface [27]. Oxides are stiff materials as compared to metals, and the energy needed to deform the lattice is relatively large. The situation changes when the oxide in the form of a thin layer is placed onto a metal surface. The metal surface helps to ease the deformation of the lattice upon perturbation. This implies that a thin film has the ability to accommodate the charge accumulated through electron transfer at a species on the film's surface by a lattice distortion, a property that a thick film may not exhibit. The physical phenomenon is called a polaronic distortion [28] and is known from semiconductor physics.

One may use this knowledge to choose combinations of materials in thin oxide film design to produce systems with specific electronic properties with respect to electron transfer, which may in turn lead to specific chemical reactivity. Take, for example, cations, anions or neutrals of one and the same element adsorbed at a surface: They show different adsorption behavior and hence will undergo very different chemical reactions! Therefore, if we succeed in designing specific support systems that promote the formation of specific charge states, we might come to the point where we design catalysts for specific reactions. Of course, under reaction conditions the situation is a bit more involved because one has to consider the presence of the gas phase as well, when we try to control the electron transfer by materials design. Clearly, the gas phase determines the chemical potential of a catalyst and thus the free energy balance. It is now evident that the phenomenon described is a manifestation of the flexibility of the system.

The way the process has been described so far is very similar to the ideas put forward by Cabrera and Mott in 1948 when they discussed the oxidation of metals [29]. They assumed that while a semiconducting oxide grows on a metal, the ability to transfer electrons by tunneling to adsorbed oxygen forming a negatively charged species leads to a field that provides the driving force for transport of metal ions from the metal-semiconductor interface to the surface to form additional layers of oxide. This process will stop as the layer becomes thicker and tunneling is no longer effective. For tunneling to be decisive the oxide film cannot be a metal because in this case it is not necessary to invoke tunneling as there are no band gaps that prohibit direct electronic communication. However, the ability, even for a metallic ultra-thin oxide film as it initially grows to distort locally to accommodate charge, which concomitantly will be stabilized by metallic screening, may still be decisive for its chemical reactivity.

## Specific Examples

### 1) *Ultra-thin films grown on metal supports*

The most prominent example in the literature showing a pronounced SMSI effect via the formation of an oxide film overgrowing the metal particles is Pt/TiO<sub>2</sub> [10]. Employing model systems, where Pt (as well as Pd) particles have been deposited onto TiO<sub>2</sub>(110) single crystal surfaces and annealed to elevated temperatures, it has been shown by scanning tunneling microscopy (STM) with atomic resolution that top facets of the Pt (Pd) particles are covered by a well-ordered, ultra-thin oxide layer of a very complex structure [13,14,30-32]. There is currently much debate about whether the structures observed are complete titania layer or an intermetallic-like alloy. In addition, a large diversity of structures (including one observed on the titania supported metal particles) were obtained in the course of growth of titania ultra-thin films on Pt(111) [13,32]. Therefore, linking structure and reactivity for this system is difficult, to date. Instead, we address this issue by studying another model system, namely Pt/Fe<sub>3</sub>O<sub>4</sub>(111), which features basically the same SMSI effect [33,34].

It has been shown that annealing of Pt/Fe<sub>3</sub>O<sub>4</sub>(111) in vacuum at temperatures above 800 K causes Pt particles encapsulation by an iron oxide film with the atomic structure virtually identical to a “monolayer” FeO(111) film grown on Pt(111) (see Fig. 2). It is well established that the FeO(111)/Pt(111) film consists of close-packed layers of Fe and O, stacked as O-Fe-Pt, and exhibits a Moiré pattern due to the mismatch between the FeO(111) and Pt(111) lattices [35].

Once formed this film is extremely stable and chemically inert under conditions typically applied in UHV-based experiments. It has turned out, however, that the film shows considerable CO oxidation activity when the reaction is performed at mbar-range of pressures and relatively low temperatures (~450 K) [36], where Pt(111) is essentially inactive due to the blocking effect of CO on O<sub>2</sub> dissociation [37]. The experimental results (obtained by Auger electron spectroscopy (AES), Low energy electron diffraction (LEED), Temperature programmed desorption (TPD) and STM) combined with density functional theory (DFT) calculations showed that at elevated pressures the bi-layer FeO(111) film transforms into the tri-layer O-Fe-O film as shown in Fig. 3 [36, 38]. The mechanism for this transformation includes O<sub>2</sub> adsorption on the Fe atom pulled out of the pristine FeO film from the interface to the metal (Fig. 3a). In this state electrons are transferred from the oxide/metal interface to oxygen, resulting in a superoxo

species, which then dissociates, ultimately forming a O-Fe-O tri-layer structure (Fig. 3b). This reaction is computed to be site specific within the Moiré unit cell, and as such may explain STM results showing the formation of close-packed FeO<sub>2</sub> islands rather than a continuous FeO<sub>2</sub> film [39].

The topmost O atoms are more weakly bound as compared to oxygen in original FeO layer [38], and may readily react with incoming CO to form CO<sub>2</sub> that leaves behind an oxygen vacancy upon desorption (see Fig. 3c). The overall activation barrier for CO<sub>2</sub> formation, as determined by DFT (~0.3 eV), is considerably lower than the computed barrier for the CO oxidation reaction on Pt(111), which is of the order of 1 eV [39]. Certainly, to end the catalytic cycle, the oxygen vacancies must be replenished via the reaction with O<sub>2</sub> from the gas phase. Comparison of the CO + O<sub>2</sub> and CO + NO reactions under the same conditions revealed that the replenishment of oxygen vacancies is the rate-limiting step that proceeds much faster with O<sub>2</sub> than NO [40]. As a result, the CO + NO reaction rate is negligible as compared to CO + O<sub>2</sub>.

Turning now back to the encapsulated Pt/Fe<sub>3</sub>O<sub>4</sub>(111) system, in the light of structure and reactivity results obtained on the extended FeO(111)/Pt(111) films, one would reasonably expect higher reactivity of the encapsulated Pt particles as compared to the “naked” Pt particles. This was observed, indeed! Although the enhancement effect was found to be size dependent [41], this finding indicated that the conclusions drawn for extended film surfaces could be extrapolated to finite size systems.

The results clearly show that it is the tri-layer O-Fe-O film that catalyzes CO oxidation by providing weakly bound oxygen, whose formation only occurs at high oxygen pressures. It is important to note that both, the transformation of the FeO into FeO<sub>2</sub>-like film and the oxygen vacancy replenishment under the reaction conditions, involve the charge transfer accompanied by a lattice distortion. As highlighted above, both factors favor the reaction on ultra-thin films. Indeed, under the same conditions the reaction proceeds with the much lower rate on thicker iron oxide films, which are of Fe<sub>3</sub>O<sub>4</sub>(111) in nature [41].

While in the case of O<sub>2</sub> interacting with the FeO layer on Pt, the species, formed in the course of the formation of the reactive FeO<sub>2</sub> tri-layer, is a transient species, a stable species has been predicted to form on a thin MgO(100) layer on Ag(100)[42], which is then the active species in CO oxidation. The superoxo species is stabilized through polaronic distortion of the MgO lattice which may only occur if the film is ultrathin. In fact, the polaronic distortion manifests itself in the g-tensor components of the electron

paramagnetic resonance (EPR) signal which may be directly compared with  $\text{O}_2^-$  formed by a different mechanism on bulk MgO. This polaronic distortion is a considerably smaller than the one observed for FeO which lead to the transient species.

To verify the theoretical predictions, the interaction of the MgO(100) films with  $\text{O}_2$  have recently been studied by EPR spectroscopy [43]. The EPR results (see Fig. 4) revealed spontaneous activation of molecular oxygen forming an  $\text{O}_2^-$  radical, which was only observed on very thin films and vanished upon increasing the film thickness to the 15 monolayers (ML), i.e. in full agreement with the theoretical calculations. Note, however, that the reaction probability and the abundance of the  $\text{O}_2^-$  formed is small and so it has not been possible so far to quantify the reactivity.

The reaction mechanism suggested for the MgO(100) films is hardly possible for the FeO/Pt system with a very high work function which renders the electron transfer to species on the film surface quite unlikely. In fact, the activation of oxygen initiating the FeO  $\rightarrow$  FeO<sub>2</sub> transformation is only possible due to a local lowering of the work function by  $\sim 1.5$  eV when the Fe cation is pulled out from the oxide-support interface into the top layer. Based on these considerations, and bearing in mind that for the ultra-thin films the work function is basically determined by the substrate underneath the film, one could, in principle, tune the reactivity of the oxide films by changing the metal support, provided, however, the oxide film grows with the same structure, which is not obvious *per se* since the choice of a metal substrate for the growth of a particular oxide film is intimately related.

Following those ideas, we have recently initiated studies on iron oxide films grown on Pd(111), that has almost an identical lattice constant as Pt(111), i.e. 2.75 and 2.78 Å, respectively, but a considerably lower work function, i.e. 5.6 vs 6.1 eV, respectively. The prepared monolayer films on Pd(111) showed structural (LEED, AES, STM) characteristics [44] very similar to the FeO(111)/Pt(111) film. The films were then examined with respect to the CO oxidation reaction under the same reaction conditions as previously studied on FeO/Pt(111) films (10 mbar CO + 50 mbar  $\text{O}_2$  at 450 K). Again, the FeO(111) film on Pd(111) showed higher  $\text{CO}_2$  production than the bare Pd(111) surface, thus supporting the conclusion on the promotional effect of thin iron oxide films in low temperature CO oxidation. However, the observed rate enhancement was considerably lower than in the case of FeO(111)/Pt(111), which sounds counterintuitive if only considerations on work function were decisive. What do we expect based on the ideas presented above? On the one hand, the lower work function would facilitate the



formation of  $\text{Fe}_3\text{O}_4$ . On the other hand, this may result in a stable  $\text{FeO}$  species without alteration of the Fe-O stacking sequence which is necessary for the formation of the reactive, O-Fe-O film (see Fig. 3a). This, in turn, would lead to deactivation with respect to FeO/Pt(111) and might explain the observation, but certainly additional experimental studies are necessary to elucidate the atomic structure of the FeO/Pd films at elevated pressures.

One may notice that the O-Fe-O stoichiometry of the film implies Fe atoms in the formal oxidation state 4+, which is very uncommon for the iron oxides and the DFT calculations actually show that the oxidation state is close to 3+ due to the presence of the metal substrate. However, there are, of course, transition metals which favor the required,  $\text{MO}_2$  stoichiometry such as  $\text{MnO}_2$  and  $\text{TiO}_2$ . Their reactivity when prepared as ultrathin films may be of interest, therefore. The preparation of  $\text{MnO}_2$  films with the tri-layer O-Mn-O structure has recently been reported on Pt(111) [45]. Moreover, it has been shown that this film possesses more weakly bound oxygen than in the monolayer MnO(111) film, but reactivity has not been studied, yet. Regarding ultrathin films of  $\text{TiO}_2$  the situation seems to be more complicated since several different structures, often coexisting, have been observed on Pt(111) [32]. Nevertheless, the preparation of ultrathin oxide films is extensively growing field that makes the expectations quite promising.

To sum up, the above examples demonstrate that ultra-thin oxide films may enhance reactivity of metal catalysts, particularly in oxidation reactions in the low temperature regime, where pure metal catalysts may suffer from site blocking effects and strong chemisorption of reactants.

## *2) Native oxide films on metals*

The above section dealt with oxide films of one metal grown on a consisting of a second metal support. The question, which may be raised now, is whether the same picture as developed above holds true for native metal oxide films. In essence, there is nothing that would change the underlying physical principles. Under net oxidizing conditions and relatively high temperatures, even noble metals like Pt and Ag could, in principle, have surface oxide layers that may affect reactivity or even be the active phase in a reaction. Perhaps, the most explored and still controversially discussed example concerns CO oxidation over ruthenium catalysts which recently attracted attention of the catalytic and surface science communities.

Considering model studies only, several oxygen containing surface structures (collected in Fig. 5) have been suggested as the most active: (i)  $O(1\times 1)$ -Ru(0001) virtually formed only at high oxygen pressures; (ii) a crystalline  $\text{RuO}_2(110)$  film about 1 nm in thickness on metallic Ru(0001); (iii) ill-defined transition surface oxides [16-24]. Each model has its own pros and cons. It is fair to say, that the experimental results critically depend on the surface preparation and reaction conditions (pressure, temperature,  $\text{CO}/\text{O}_2$  ratio). Mass transport effects bring additional complexity into such studies and become more critical at atmospheric pressures [46]. Therefore, direct comparison of the results obtained in different research groups is often difficult if not impossible. It is generally believed that high catalytic activity is intimately connected with a disordered dynamic phase with significant compositional fluctuations. This conclusion is qualitatively similar but not as specific as the conclusions presented in the previous section.

The initial stages of the oxide formation on Ru(0001) have been addressed by DFT [47]. The results suggested that oxygen first occupies the surface hcp sites in amounts up to one monolayer (ML), and only then the additional oxygen goes sub-surface, where it preferentially forms islands with a local  $(1\times 1)$  periodicity and ultimately the hexagonal O-Ru-O structure (see Fig. 6). The total energy may be further minimized by a small lateral displacement (stretch) of the O-Ru-O layer that is relatively weakly coupled to the underlying metal. From a thermodynamic point of view, such process can, in principle, be continued until a critical film thickness (equivalent to  $\sim 5$  ML of oxygen) is approached, where the transformation towards the thermodynamically more stable  $\text{RuO}_2(110)$  structure occurs.

To the best of our knowledge, systematic studies of the reactivity of  $\text{RuO}_x$  films as a function of the film thickness have not been performed. A study that comes closest has been a low energy electron microscopy (LEEM) study [49] on oxidation of Ru(0001) (albeit at low pressures) indicating the *co-existence* of  $\text{RuO}_2(110)$  domains and a disordered, trilayer-like O-Ru-O-O surface oxide over a wide range of temperature and gas phase conditions, i.e. in variance to the previous view on surface oxides as a metastable precursor to the  $\text{RuO}_2(110)$  thin film oxide. Both structures rapidly and uniformly react with CO and can be reoxidized in  $\text{O}_2$ . This behavior was taken as an indication of high CO oxidation activity, which was shown to be much higher than observed on  $(1\times 1)$ -O phase.

There is still debate on which is the more active phase and at which temperature, while all groups agree that the binding energy of oxidizing oxygen has to be sufficiently small

to render the system active. So far, in modeling the reaction theory has only treated CO oxidation on the stoichiometric RuO<sub>2</sub>(110) surface and not considered ultra-thin films. Neither has theory investigated the process of creating the trilayer film as well as the stoichiometric surface. Therefore, a direct comparison of mechanism occurring on the O-Fe-O and O-Ru-O films is not possible at present.

The “ruthenium puzzle” triggered a closer look and more elaborative studies on other platinum group metal catalysts operating in oxygen ambient. Certainly, ruthenium has much higher affinity to oxygen as compared to the noble metal catalysts, such as Rh, Pd and Pt widely used in oxidation of exhaust gases, volatile organic compounds, etc. Indeed, dissociative adsorption energies of oxygen are of 334, 234, 230 and 188 kJ/mole for the close-packed Ru, Rh, Pd and Pt surfaces, respectively, which correlate with standard heats of formation for RuO<sub>2</sub>, Rh<sub>2</sub>O<sub>3</sub>, PdO and PtO<sub>2</sub> (-153, -119, -116 and -71 kJ/mole, respectively) [49]. Albeit the formation of surface oxide films on Rh, Pd and Pt in the oxygen ambient is less favorable, this is not impossible *per se* at the high chemical potential of oxygen. Several studies have recently been reported on the oxidation of noble metals, in particular for the more open surfaces such as (100) and (110), which are known to be far more reactive towards oxygen than (111). Those studies will be surveyed below.

Employing STM inside a high-pressure flow reactor allowed *in situ* recording both, the morphology of the Pt(110) surface and its reactivity in CO oxidation [50]. Switching from CO to O<sub>2</sub> flow (0.5 bar, 425 K) and back caused reversible extensive roughening of the Pt surface which was interpreted in terms of the formation of a thin platinum oxide film accompanied by the high CO<sub>2</sub> production presumably through a M-vK mechanism. According to DFT studies [50] which followed the initial experimental investigations the surface oxides on Pt(110) are metastable and must be stabilized, e.g. by defects and/or kinetic restrictions.

Further *in situ* studies using surface x-ray diffraction (SXRD) [52] suggested that under O<sub>2</sub>-rich conditions in the range of 425-625 K the surface is covered with the  $\alpha$ -PtO<sub>2</sub> -like oxide film, with the nominal thickness corresponding to the 2-3 stacks of an O-Pt-O triple layer. (Note also that, very recently, tri-layer  $\alpha$ -PtO<sub>2</sub> structures has been reported for the Pt(111) surface, but its formation is kinetically limited, indeed [53]). The oxide film is distorted as compared to bulk  $\alpha$ -PtO<sub>2</sub> in order to accommodate the Pt(110) surface or exhibit totally incommensurate structure. The commensurate oxide only appeared when both, O<sub>2</sub> and CO, were present in the reaction ambient at sufficiently

high temperatures. This finding was explained by DFT in terms of a stabilization effect of chemisorbed carbonate ions. Importantly both oxides showed substantially higher catalytic activity than the metallic Pt surface.

On Pd(111), two dimensional oxides were observed even at low oxygen pressures as intermediate phases between an oxygen overlayer and bulk PdO [54]. Further STM, SXRD, XPS and DFT studies [55] suggested the formation of an incommensurate surface oxide of Pd<sub>5</sub>O<sub>4</sub> stoichiometry and almost coplanar geometry which has no resemblance to any bulk oxides of Pd.

The oxidation of the Pd(100) surface at low O<sub>2</sub> pressures proceeds through several steps, ultimately resulting in either a (5x5) or a ( $\sqrt{3} \times \sqrt{3}$ )R27° ordered structures, depending on the experimental conditions, both originally assigned to the single PdO layer [56]. Surprisingly, the latter structure (essentially a strained PdO(101) trilayer on Pd(100) [57]) has been observed even at 575 K and 1 bar O<sub>2</sub> in the course of SXRD studies of CO oxidation over Pd(100) at elevated pressures [58]. The formation of a ~4 nm thick, poorly ordered bulk oxide phase with predominantly PdO(001) orientation primarily occurred at higher temperatures. Significant discrepancy between the experimental and the DFT-computed stability phase diagram was rationalized on the basis of kinetic hindrance to the formation of the bulk oxide.

Again, as in the case of Pt(110), the *in situ* STM studies [59] at atmospheric pressures revealed morphological changes from adsorbate covered Pd(100) to an oxidic state depending on the CO:O<sub>2</sub> ratios. However, unlike the Pt(110) surface, where roughening was shown to be reaction induced, the Pd(100) surface became rough upon oxidation already. The CO oxidation was accompanied by further surface roughening. In the oxidic state the surface showed a considerably higher reactivity, which was proposed to proceed via the M-vK mechanism.

A temperature programmed reaction (TPR) study in the 10<sup>-8</sup> - 10<sup>-6</sup> mbar pressure range revealed that the ( $\sqrt{3} \times \sqrt{3}$ )R27° surface was essentially inert in CO oxidation [56]. The bulk-like PdO overlayer was even less reactive towards CO. The low reactivity of these structures was tentatively assigned to their inability to strongly adsorb CO. Combined with TPR, the *in situ* STM and LEED results suggested that, upon exposure to CO, the ( $\sqrt{3} \times \sqrt{3}$ )R27° structure transforms into the much more active (2x2) structure, which probably contains sub-surface oxygen. The results indicated that the inactive structures in fact supply oxygen for replenishing those from the (2x2) domains.

Nevertheless, the  $(\sqrt{3} \times \sqrt{3})R27^\circ$  surface as the best established structure of Pd-oxide layer on Pd has been considered in a DFT analysis of CO oxidation on Pd(100) [60]. The results suggested that the monolayer oxide film might indeed be a relevant structure for the CO oxidation reaction on Pd(100) at technological relevant pressures. Further first-principles kinetic Monte Carlo simulations revealed that local pressure and temperature fluctuations may induce a continuous formation and decomposition of oxidic phases during steady-state reaction such that both, oxidic and reduced states become important for the reaction.

Finally, well-ordered ultrathin oxide films form on Rh surfaces [61-63]. In particular, combination of high resolution XPS, STM, SXRD and DFT revealed the self-limited growth of an O-Rh-O trilayer film on Rh(111) at intermediate oxygen pressures [62]. The film forms a coincidence superstructure very similar to FeO(111)/Pt(111), as depicted in Fig. 7. However, based on the DFT results, this surface oxide is only a transient, kinetically stabilized structure. A thick corundum-like Rh<sub>2</sub>O<sub>3</sub> bulk oxide, which is thermodynamically more stable, forms at significantly higher pressures and temperatures, e.g. 10 mbar and 800 K. Interestingly, the similar O-Rh-O films were observed on Ru(100) and even on highly stepped Rh(553) and Rh(223) surfaces, where the original step structure of the metal single crystal completely vanished upon oxidation [63].

Recent combined SXRD and reactivity (mass spectrometry) studies of the Rh(111) surface provided strong evidence that the tri-layer surface oxide is much more active than metallic Rh in low temperature (ca. 500 K) CO oxidation, whereas the Rh bulk oxide was not active at all [63]. Although the authors could not rule out from their experiments the coexistence of the surface oxide and metallic surface as responsible for the highest reactivity, there definitely is a close similarity in the structure-reactivity relationship between the RhO<sub>2</sub>/Rh and the previously discussed FeO<sub>2</sub>/Pt systems.

### **Concluding remarks**

Ultrathin metal oxide films turn out to exhibit interesting properties. While in the past oxide films covering metal surfaces had been considered detrimental for catalysis, as suggested by the observation of the SMSI-induced encapsulation of metal particles on the reducible oxide supports. With the recent evidence culminating, there are also clear indications that oxide overlayers may enhance activity for CO oxidation over the supporting metal, in particular temperature ranges. The mechanism of formation of the

active oxide film is not evident in all cases, but it seems, that the formation of rather weakly bound oxygen is a crucial factor in rendering the oxide film formed under reaction condition an active one. While in most cases a clear identification of the details of formation and reaction of the active film has not been possible, the case of FeO on Pt allowed us to unravel both, the mechanism of formation of the active film, its structure, and the rate determining step in CO oxidation. In most other cases experimental and theoretical studies have mainly concentrated on structural aspects of various phases formed not on the mechanism of formation and structural changes according under reaction conditions. We believe that a continuously growing body of studies on structure and reactivity of ultrathin oxide films in conjunction with potentially interesting target reactions could ultimately result an avenue leading to the rational design of the “monolayer” oxidation catalysts, which are in essence metal supported monolayer oxides in nature. This is equivalent to a concept that has been put forward several decades ago [64,65] without having the tools at hand to prove it.

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## Figures

Figure 1. Schematic representation of an ultrathin oxide film, grown on a metal, reacting with ambient gases through the charge transfer to adsorbed species accompanied by the lattice distortion.

Figure 2. Scanning tunneling microscopy image (presented in the differentiated contrast) of Pt particles deposited onto Fe<sub>3</sub>O<sub>4</sub>(111) and annealed in vacuum at 850 K. Inset shows atomically resolved STM image of the top facet showing a 3 Å periodicity and long-range superstructure assigned to the formation of an FeO(111) layer on Pt(111) as schematically shown.

Figure 3. (a) Steps in transformation of bi-layer FeO(111) into the tri-layer O-Fe-O film at high O<sub>2</sub> chemical potentials as predicted by DFT. (b) Final structure. Fe blue, O red, Pt gray. (c) Typical reaction kinetics of CO<sub>2</sub> production on FeO/Pt(111) and Pt(111) surfaces (40 mbar CO, 20 mbar O<sub>2</sub>, He balance to 1 bar, 450 K). The reaction proceeds through a Mars-van Krevelen -like mechanism as schematically shown.

Figure 4. EPR spectra taken for 20 L O<sub>2</sub> (1 L = 10<sup>-6</sup> Torr sec) adsorbed at 30 K on a 4 ML thick MgO(001) film grown on Mo(001) as a function of the polar angle  $\theta$  (see top right for definition). The magnetic field was oriented in a plane spanned by a direction equivalent to [100] in the surface and the surface normal. On right: top and cross views of the adsorption geometry (O<sub>2</sub> ovals). Bottom right: calculated adsorption geometry (O blue, Mg yellow, Ag grey).

Figure 5. Schematic representation of the oxidation states of Ru(0001). (a) (1x1)-O adsorption phase with a ~ 1 ML oxygen; (b) transient surface oxides, RuO<sub>x</sub>, with oxygen incorporated into the subsurface layers; (c) rutile RuO<sub>2</sub>(110) phase. Ru blue, O red.

Figure 6. Atomic geometries of the O–Ru–O trilayer (on left) and the RuO<sub>2</sub>(110) structure (on right). Top and perspective views are shown with the surface unit cells indicated. The rutile structure is achieved by expanding the trilayer in the directions indicated by the arrows. (Reproduced from Reuter et al. Chem. Phys. Lett. 352 (2002) 311).

Figure 7. Side and top views of the most stable, O-Rh-O surface oxide as calculated by DFT. The inset shows the simulated STM image. Reproduced from Gustafson et al, Phys. Rev. Lett. 92 (2004) 126102.