PERSPECTIVE

Strong Metal–Support Interaction and Reactivity of Ultrathin Oxide Films

Shamil Shaikhutdinov[1]

Abstract

Noble metal particles supported on transition metal oxides (TMO) may undergo a so-called strong metal–support interaction via encapsulation. This perspective addresses catalytic properties of the metal catalysts in the SMSI state which can be explained on the basis of complementary studies performed on well-defined, metal-supported TMO films. In particular, the results of low temperature CO oxidation revealed the key role of weakly bound oxygen species provided by a two-dimensional ("monolayer") oxide film. The binding energy of such oxygen atoms can be used as a descriptor for oxidation activity. Reaction rate enhancement often observed for TMO films partially covering the metal surface is rationalized within a mechanism in which the metal acts as a promoter to create the most active "$oxide_{red}/oxide_{ox}$" interface formed by reduced and oxidized phases in the film. Although only low temperature CO oxidation is considered, it is tempting to generalize these ideas to other oxidation reactions following the Mars–van Krevelen type mechanism. In addition, metal-supported ultrathin TMO films may serve as well-defined model systems to examine different aspects of the "electron theory of catalysis" which was proposed long ago and which is based on electron transfer mechanisms.

Graphical Abstract
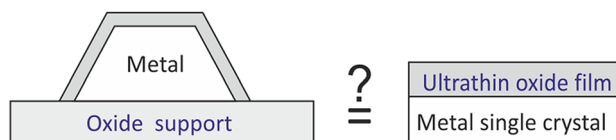
1 Introduction

The term strong metal–support interaction (SMSI) is commonly associated with the original works of Tauster and co-workers from the late 1970s, who observed that the uptake of H_2 and CO drops after some treatment of oxide-supported noble metal catalysts, most markedly for Pt supported on TiO_2 [1, 2]. As a possible explanation, the authors first suggested electronic effects via charge transfer and even rejected

metal encapsulation which is now considered as the main manifestation of SMSI, based on recent advanced electron spectroscopy studies [3, 4]. SMSI is sometimes used in a more general sense by including support effects on metal dispersion, spatial distribution, and particle shape. Although the Pt/TiO_2 system remains the classic example of SMSI via encapsulation, several other combinations of reducible transition metal oxides (TMO) and metals have shown similar behavior [5–8]. Despite enormous efforts to directly visualize the encapsulation process, the precise mechanism of encapsulation remains unknown. Thermodynamic considerations favor oxide spillover onto the metal surface rather than migration through the metal particle and subsequent segregation to the surface. Considering only the final structure of a catalyst in such a state, we are left, in essence, with

✉ Shamil Shaikhutdinov
shaikhutdinov@fhi-berlin.mpg.de

1   Abteilung Chemische Physik, Fritz Haber Institut der Max Planck Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany

a system consisting of a thin oxide film fully or partially covering a metal particle. Accordingly, the morphology and chemical composition of the oxide overlayer can be rationalized on the basis of results obtained for the growth of thin oxide films on metal substrates. In the absence of kinetic effects, the growth mode is determined by a balance between the surface free energies of the oxide, the metal and of the metal/oxide interface [9, 10]. Note, however, that ambient gases may additionally affect the final structure. Since the surface energies of TM oxides are considerably smaller than those of catalytically relevant metals, one expects that the oxide will wet the metal surface. Of course, if the encapsulating oxide film is thick, e.g. a few nanometers, such metal particles "buried" by the oxide support will not be involved in the catalytic reactions. However, when the oxide layer thickness is comparable to the oxide lattice constants the situation is not as straightforward and intriguing effects appear. Henceforth, we refer to such films as "ultrathin", "two-dimensional (2D-)", or "monolayer" films. An even more complicated picture develops if the metal surface is only partially covered, either by small patches of a 2D-oxide film or oxide nanoparticles. Therefore, one may reasonably

assume that the catalytic properties of TMO supported metal catalysts in the SMSI state (via encapsulation) is intimately linked with the structure and reactivity of metal-supported ultrathin TMO films. This is the focus of the present Perspective.

Well-ordered oxide films grown on metal single crystal surfaces have long been used as planar model systems for studying chemical reactions at oxide surfaces and of metal nanoparticles deposited on them. Such systems facilitate the use of the experimental tools of surface science which are often based on the use of charged particles (ions or electrons) [9, 11–13]. In the course of such studies, it has been found that ultrathin films often show structures and properties different from their bulk counterparts and "thick" films [14–19]. Therefore, to understand catalytic reactions over a catalyst which underwent encapsulation, one needs to understand the reactivity of ultrathin oxide films. In the following, some examples will be discussed to validate this approach.

Fig. 1 Cross-sectional TEM (**a, b**) and STM (**c**) images of Pt particles deposited on $Fe_3O_4(111)$ at 300 K and then annealed to 850 K in UHV. **d** Schematic view of an encapsulated Pt particle, and a side view of the FeO(111)/Pt(111) film
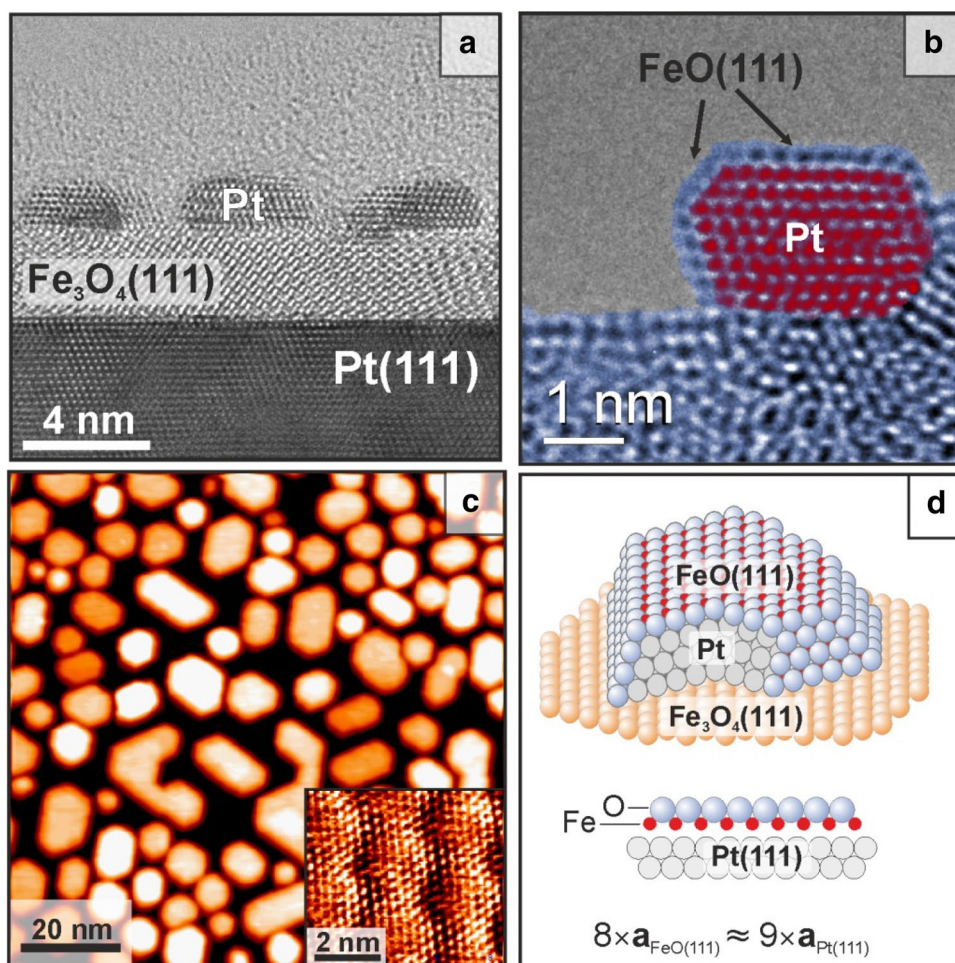
2 Discussion

Figure 1 shows scanning tunnelling microscopy (STM) and transmission electron microscopy (TEM) images of Pt particles deposited onto a crystalline $Fe_3O_4(111)$ film grown on Pt(111) and then vacuum-annealed at 850 K. The images show well-faceted Pt particles exposing primarily the (111) surface [6, 20]. CO uptake measured by temperature programmed desorption (TPD) drops to almost zero upon high-temperature annealing, and as such the system manifests the classic SMSI effect. The STM images of the top facets revealed a hexagonal lattice of protrusions with an ∼ 3 Å periodicity and a superstructure with an ∼ 25 Å periodicity, which is clearly seen on large particles. This structure was assigned to a well-known monolayer thick FeO(111) film. Preparation of such films on Pt(111) and Pt(001) substrates was initiated by Somorjai and coworkers in the early 1990s [12, 21]. Further evidence for Pt encapsulation came from cross-sectional high-resolution TEM studies [20] as shown in Fig. 2a, b.

As another example, we refer to STM studies of Pt deposited onto a $TiO_2(110)$ single crystal [22]. Upon high temperature annealing in vacuum, the top facets of Pt particles showed structures virtually identical to those obtained for ultrathin TiO_x films grown on Pt(111) [23]. Although the precise atomic structures remain under debate, this example provides further evidence that oxide overlayers formed upon encapsulation of metal nanoparticles bear close resemblance and may even be virtually identical to the ultrathin oxide films prepared on the respective metal surfaces.
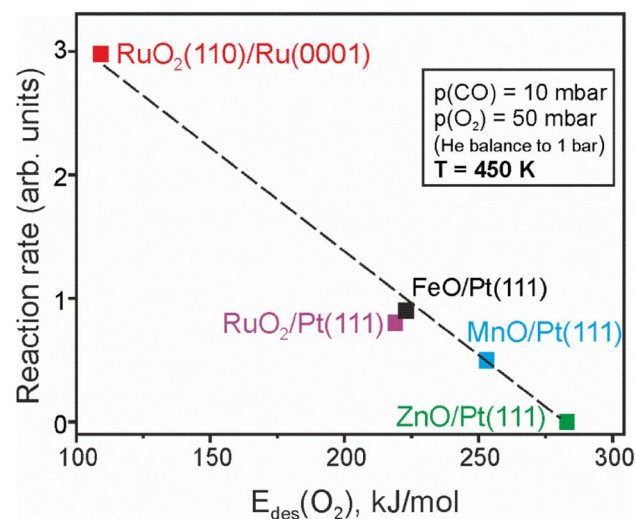
In the case of the $Pt/Fe_3O_4(111)$ system, which were studied in the CO oxidation reaction at nearly atmospheric pressures, the encapsulated Pt particles showed a considerably higher reaction rate than the uncovered Pt particles prepared at low temperatures [24]. This somewhat unexpected finding demonstrated that encapsulation, which is commonly thought to have a detrimental effect on reactivity, may actually promote a reaction. To rationalize this effect, we studied the structure–reactivity relationships of FeO(111) films on Pt(111). At low temperatures (i.e., below 500 K), the Pt(111) surface shows negligible activity due to the blocking of O_2 dissociation by adsorbed CO. The FeO(111) film, on the other hand, showed much higher activity over a wide range of the $CO:O_2$ ratios in the reaction mixture, most markedly in excess of O_2 [25]. Therefore, it is the formation of an FeO(111) monolayer film on Pt particles that is responsible for the enhanced reactivity of $Pt/Fe_3O_4(111)$ in the SMSI state.

Before we address the reaction mechanism, let us first recall that a monolayer FeO(111) film consists of close-packed layers of iron and oxygen stacked as O–Fe–Pt(111) (see Fig. 1d). The Moiré structure originates from the ∼ 10% mismatch between the Pt(111) and FeO(111) surface lattices. The polar oxide surface is stabilized by strong inward relaxation of the Fe and O layers accompanied by considerable charge transfer to the Pt atoms at the interface. The film is very stable and chemically inert in UHV conditions. However, at higher oxygen chemical potentials, the FeO(111) film transforms into a structure where O–Fe–O tri-layer domains of local FeO_2 stoichiometry form a close-packed structure that follows the Moiré pattern as a template [26] (see below). Note that the Fe ions in the FeO_2 film are in the 3+ oxidation state due to electron transfer from the underlying Pt substrate [27].

When compared to the original FeO(111) film, the FeO_{2-x} film possesses a much more weakly bound oxygen species which were revealed by TPD via a low temperature desorption peak that has tentatively been associated with the O atoms in the topmost layer of the FeO_2 tri-layer, although the desorption mechanism remains unknown. Therefore, it is the formation of this weakly bound oxygen (WBO) at the oxide surface that likely promotes the CO oxidation reaction. A comparative TPD study [28] of various TMO films further linked the catalytic activity with the state of oxygen in the "oxygen-rich" films (i.e. treated in pure oxygen atmosphere). These studies showed that the weaker the surface oxygen is bound, the higher the reaction rate is (Fig. 2). Thus, the desorption temperature of WBO species can be used as a good descriptor for oxidation activity to first approximation. Since CO adsorbs weakly on almost all oxide surfaces, its adsorption properties do not differ drastically for various oxides, at least for the closed films. Moreover, reactivity studies of FeO(111) monolayer films grown on Au(111) revealed a

Fig. 2 CO oxidation rate measured on various thin films (at reaction conditions as indicated) as a function of desorption energy of weakly bound oxygen (WBO) measured by TPD on oxidized films

direct correlation between the total amount of WBO species in the sample and the reaction rate [29]. Although the atomic structure of the "O-rich" films on Au(111) remains unclear and may differ from that on Pt(111), the results further point to weakly bound surface oxygen as the key species in the CO oxidation reaction.

The observed relationship between the reaction rate and O_2 desorption temperature favours a Mars–van Krevelen (MvK) type mechanism: The CO_2 molecule formed by the $CO + O$ reaction desorbs and leaves an oxygen vacancy behind, which is then filled by O_2 from the gas phase to complete the catalytic cycle. On the basis of density functional theory (DFT) calculations performed on a continuous FeO_2 tri-layer film on Pt(111), it was concluded that the reaction takes place between CO in the gas phase and O in the film, i.e. via the Eley–Rideal (ER) mechanism. In most cases, however, CO oxidation at surfaces follows the Langmuir–Hinshelwood (LH) mechanism, i.e. the associative reaction of adsorbed CO with O atoms formed by O_2 dissociation. For the case of oxide surfaces terminated by oxygen, the reaction may, in fact, be triggered by the ER mechanism that opens up the metal cationic sites and thus provides conditions for the LH mechanism in the steady state via CO adsorption on metal sites and reaction with the surrounding oxygen species. For the FeO(111)/Pt(111) system, such a scenario suggests that CO first reacts with topmost oxygen in the O–Fe–O tri-layer, ultimately creating oxygen vacancies and hence exposing Fe cations for CO adsorption.

Let us now address the case of metal surfaces partially covered by an oxide film. In fact, such studies were used in the past to understand the role of oxide promoters on noble metal catalysts, in particular in CO and CO_2 hydrogenation reactions [30]. The results showed a maximum activity at sub-monolayer oxide coverage, scaled with the length of the perimeter at the oxide/metal boundary, and was therefore assigned to reactions taking place at the oxide/metal boundary. These so-called "inverse" [31–33], i.e. oxide-on-metal, model catalysts were used for elucidating reaction mechanisms in conventional, i.e. metal-on-oxide, catalysts, assuming that the metal-oxide interfacial structures are similar. With the help of STM, it was found, however, that oxide deposits on metal single crystals often form patches of ultrathin oxides with many different structures and complex phase diagrams [15, 17]. In this respect, ultrathin films of iron oxide show only one stable phase, i.e. FeO(111), on many noble metal surfaces (Pt, Pd, Au), which simplifies establishing structure–reactivity relationships.

The first results of Bao and co-workers for CO oxidation on FeO(111) islands on Pt(111) in UHV conditions were rationalized in terms of the reaction occurring at the FeO(111)/Pt(111) interface [34]. The mechanism was investigated with DFT calculations for several TMO(111) monolayer films supported on Pt(111) [35]. The calculations showed that O_2 can dissociate on coordinatively unsaturated Fe sites at the interface resulting in O atoms bonded to both Fe and Pt, which then react with CO adsorbed on Pt to produce CO_2. Although such a mechanism seems plausible under UHV conditions, it hardly holds true for higher pressures where the tri-layer FeO_{2-x} phase forms.

CO oxidation on partially covered FeO(111)/Pt(111) films at near atmospheric pressures and 450 K revealed a maximum activity for films covering about 40% of the Pt(111) surface. This indicates that the oxide/metal interface is, indeed, more active than the oxide surface itself [36]. In addition, TPD studies of CO adsorbed on O-rich (i.e., FeO_{2-x}) films also showed a maximum in CO_2 production at ~40% coverage, whereas the TPD results on "as prepared" sub-monolayer FeO(111) films only showed fingerprints of CO oxidation on bare Pt(111). Therefore, the enhanced reactivity was reasonably assigned to the reaction between CO adsorbed on Pt and oxygen species adsorbed at the edge of FeO_{2-x} (and not of FeO) islands. In principle, one could not rule out that the FeO(111) bilayer remains stable in the highly reducing ambient conditions applied, for example, in PROX (preferential CO oxidation in excess of hydrogen) [37]. However, the role of hydroxyls and water in this reaction remains to be investigated in detail.

Nonetheless, both proposed structures for the most active phase infer that the reaction occurs at the metal/oxide interfaces, either FeO_2/Pt or FeO/Pt. However, a very recent study by Zhang et al. [38] provides some solid evidence that the catalytic reaction, in fact, takes place at neither interface, but instead at the boundary between reduced and oxidized phases of the film, in other words, at the $oxide_{red}$/$oxide_{ox}$ interface.

Figure 3 displays STM images of FeO_{2-x} islands, where periodic protrusions of ~2 nm in diameter follow the Moiré structure of the original FeO(111) film and are assigned to FeO_2 tri-layer domains. These are shown in side view in Fig. 3a [27]. CO exposure at 350–450 K reduces the FeO_{2-x} phase back to FeO(111), even at pressures of 10^{-6} mbar. Time-lapse ex situ STM imaging showed that the reaction starts at the island edges and propagates into the interior [38]. Interestingly, the Moiré pattern is not lifted uniformly, but instead from the side that is closer to the island edge (Fig. 3b). This suggests that the reaction is initiated at the interface with Pt, and then continues by CO reacting at the interface between the oxidized FeO_{2-x} phase and the reduced, FeO(111)-like phase left behind (Fig. 3c). Basically, the same mechanism is observed in CO and O_2 reaction mixtures. Even in excess O_2, the regions closest to the island edges undergo reduction, while the interior remains intact. Although in O_2-rich atmospheres reduction does not propagate far from the island edge, it is clear that the initial FeO_{2-x}/Pt interface does not exist anymore under the reaction conditions that provide sustained CO_2 production
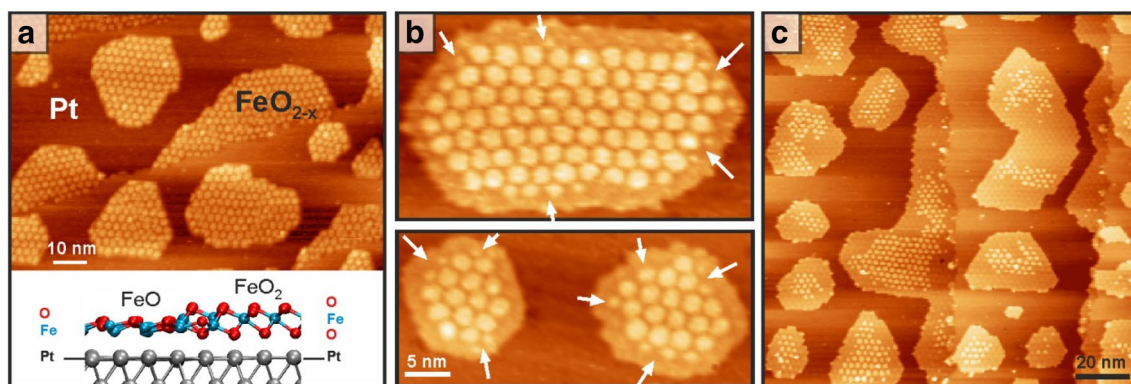
Fig. 3 STM images of the FeO_{2-x} islands on Pt(111): as prepared (**a**); after short (**b**) and long (**c**) time exposures to 10^{-6} mbar of CO (**c**). Inset in **a** shows a side view of the FeO_{2-x} film consisting of FeO_2 tri-layer domains following a Moiré structure of FeO(111)/Pt(111) as a template
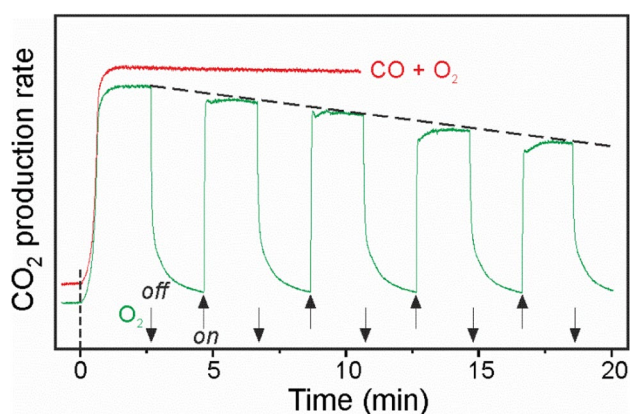

Fig. 4 CO_2 production rate measured on a sub-monolayer FeO_{2-x} film on Pt(111). At time zero, the sample was heated up to the reaction temperature 450 K with a rate 2 K/s. The red curve shows CO_2 production in the mixture consisting of 10^{-6} mbar of CO and 5×10^{-6} mbar of O_2. Green curve shows CO_2 transition kinetics by switching O_2 flow off and on, as indicated by the arrows, while keeping the CO pressure constant

(Fig. 4). When the oxygen flow is stopped, the CO_2 production drops to zero, and recovers after re-introducing O_2. However, the reaction rate is reduced upon cycling O_2 flow on and off. Bearing in mind that the FeO_{2-x} islands in pure CO ambient (i.e. in the absence of O_2 in the flow) exhibit reduction that propagates from its edge towards the island interior (see Fig. 3), the reduction of the rate can readily be assigned to a decrease of the total perimeter length of the active $oxide_{red}/oxide_{ox}$ boundary.

One may argue that the chemical potential of O_2 at low pressures used in these experiments is too low to efficiently replenish the O atoms, consumed by the fast reaction between CO on Pt and O at the edges of oxide islands, and hence too low to preserve the FeO_{2-x}/Pt interface from the reduction propagating inside the island. On the other hand, a very similar oxide morphology was observed on dense

FeO(111) films by consecutive exposures first to O_2 and then to CO in the mbar pressure range [39]. In Fig. 5, one can easily recognize patches of FeO_{2-x} surrounded by the reduced phase. Also, cut Moiré spots at the domain's edge resemble those shown in Fig. 3b obtained at 10^{-6} mbar pressure. The formation of the reduced phase in the dense films is probably triggered at defects, whereas it readily occurs at the islands edges thanks to the reaction with CO adsorbed on Pt. Therefore, the volcano-type activity *vs* coverage plot [36] may be attributed to a facile formation of the $oxide_{red}/oxide_{ox}$ interface in vicinity of the oxide/metal boundary rather than to the catalytic reaction at the boundary itself.

The proposed mechanism agrees well with the DFT calculations of the oxygen vacancy formation energy [36]. Yet not all hypothetical structures have been computed, the lowest energy (1.36 eV) is obtained for the O atoms at the FeO_2/FeO interface in the FeO_{2-x} film (see Fig. 3a). Note, however, that this interface is not identical, to the $oxide_{red}/oxide_{ox}$ interface formed during the CO oxidation reaction, otherwise the reaction would occur homogeneously across the film, which is not the case. For comparison, the respective energies for O atoms at FeO_2/Pt (1.53 and 1.58 eV) are considerably higher, which are, in turn, lower than those computed for the topmost oxygen in the FeO_2 trilayer (1.67 eV). These are all much more weakly bound than O atoms at the FeO/Pt interface (2.15 eV). Therefore, the DFT calculations nicely corroborate the key role of WBO species in this reaction.

It is worth mentioning that recent studies on CoO(111) islands, grown on Au(111) and Pt(111) and considered as model catalysts for the oxygen evolution reaction [40, 41], revealed close similarities to FeO(111) with respect to the oxygen induced transformations and interaction with water [42]. Even though the CoO(111) films have not yet been studied in catalytic reactions, this finding allows generalization of the principles underlying the formation and reactivity of "tri-layer" TMO films.

Fig. 5 STM images of a dense FeO(111)/Pt(111) film after sequential exposure first to 50 mbar of O_2 and then 10 mbar of CO at 450 K for 10 min each
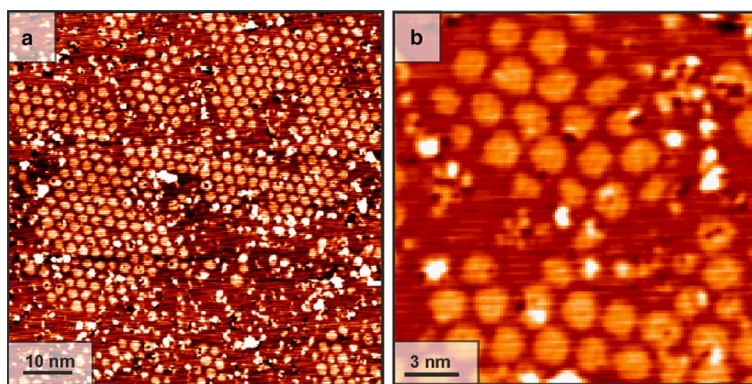
Among the thin films studied in CO oxidation, ZnO(0001) films were the least active (Fig. 2). In principle, this may be related to the fact that ZnO is not a reducible oxide, and that the formation energy of an oxygen vacancy is relatively high [43]. Another reason can be related to the fact that the ultrathin ZnO films relax into a graphene-like structure. However, the CO_2 production rate considerably increases on ZnO monolayer films on Pt(111) at sub-monolayer coverage [44]. Again, this finding has been interpreted as direct evidence for the reaction occurring at the metal/oxide boundary, although STM studies revealed structural transformations at near atmospheric pressures resulting in ZnO bilayer sheets. Such a rate enhancement was not observed for ZnO bilayer islands grown on Ag(111) [45]. In fact, ZnO deposits suppressed the reactivity of a pure Ag(111) substrate. The support effect was reasonably explained by a much stronger CO adsorption on Pt(111) compared to Ag(111) which increases its residence time and hence probability for CO to react with oxygen at the island edge. However, in the light of the reaction mechanism proposed above for the FeO films, one cannot rule out that Pt eases the formation of the reduced oxide phase at the edge of bilayer ZnO sheets and hence provides conditions for sustained reaction on the oxide surface. Yet the results available to date for ZnO(0001) films do not allow to support or exclude this hypothesis.

So far we discussed systems where a TMO film was artificially grown on a noble metal surface or was formed as a result of encapsulation. However, catalysis on bimetallic or alloy particles containing TM may also result in such systems, even in the absence of SMSI, if the reaction takes place under net oxidizing conditions. In excess oxygen, surface segregation and subsequent oxidation of the least noble metal in the bimetallic particle (i.e. TM) is highly possible. The resulted oxide layer may fully or partially cover the metal particle surface, eventually forming a core–shell structure similar to a particle formed via encapsulation. For example, such a model could be considered to explain the promotional role of Fe added to Pt/Al_2O_3 catalysts used for PROX [46].

It is generally believed that only reducible TM oxides, either as a support or as additives, have a promotional effect on catalysis by metals. Although there seem to be no systematic studies, alumina and silica (as the classic non-reducible oxides) deposited on metal surfaces will most likely block catalytic reactions. Moreover, metal catalysts supported on Al_2O_3 and SiO_2 show no SMSI effects. Nevertheless, the "ultrathin film" approach can be applied to alumina (silica) supported metal catalysts in strongly oxidizing conditions as well. It is well-documented in the literature that at relatively high O_2 pressures and temperatures even noble metals such as Pt, Pd, and Ag may form ultrathin oxide overlayers which are considered the most active (see a short review in ref. [47]). Interestingly, these "native" oxides exhibit in some cases the tri-layer structural motif.

Perhaps the most famous example highlighting the role of native oxide films is the formation of a well-ordered RuO_2(110) film on Ru(0001), which may grow up to a few nanometers in thickness depending on the ambient conditions [48]. The results of CO oxidation performed on this system fit nicely the general trend shown in Fig. 2. In this respect, it is worth mentioning that the correlation between oxygen binding energy and catalytic activity was reported long ago for pure oxide catalysts [49]. Such a trend obtained on different systems allows us to make a more general conclusion: The reactivity of ultrathin oxide films is, in essence, determined by its ability to provide "active" WBO oxygen, which is, in turn, linked with the ultra-thinness and/or peculiar structure of the oxide stabilized by the metal support. Indeed, the CO oxidation studies discussed above were carried out in an O_2-rich atmosphere in order to maintain the 2D character of the films, which otherwise dewet in O_2-lean conditions and slows down the reaction.[25].

The formation of thin oxide layers on metals and its possible effects on catalysis have been intensively discussed since the 1950s, most notably by Volkenstein [50] and Schwab [51]. This culminated in the so-called "electron theory of catalysis" focusing on the role of charge carriers and based, in essence, on models developed for metal/semiconductor

interfaces. It was believed that native oxide films formed on metals can be used to control charge transfer to and from surface ad-species rendering them catalytically active. Certainly, this scenario may also be applied to the TMO films formed on metals as a result of encapsulation. Interest in this theory has decreased over time until recently. It has started to receive considerable attention again thanks to the substantial development of experimental tools that allow the preparation of well-defined ultrathin oxide films.

Charge transfer processes mediated by ultrathin oxide films have already been proven, both experimentally and theoretically, for several cases of metal adsorption, most notably on MgO(001) films [52]. The process is controlled by the work function which can, in principle, be tuned by choosing a combination of an oxide and a metal [53]. As far as adsorption of gas molecules is concerned, the situation is less certain as the results are relatively scarce [54–56]. A DFT study [57] of CO oxidation over MgO(001)/Ag(001) predicted the reaction mechanism (still awaiting for experimental proof), in which oxygen reacting with CO is activated by charge transfer.

Clearly, further studies remain to be done to identify catalytic reactions which are, governed by charge transfer through the oxide film. Nonetheless, well-defined ultrathin films with a controllable thickness provide good planar models to examine such effects on catalysis.

3 Synopsis

The results discussed here in detail for the iron oxide—Pt system demonstrate that catalytic properties of TMO-supported metal particles in the SMSI state can be rationalized on the basis of complementary studies performed on metal-supported ultrathin TMO films.

In particular, the results of low temperature CO oxidation revealed the key role of weakly bound oxygen species in the reaction. Although only CO oxidation was considered, it is tempting to generalize these ideas to other oxidation reactions that follow a Mars–van Krevelen mechanism.

Reaction rate enhancement observed for TMO films partially covering the metal surface is commonly attributed to reactions occurring at the interfacial sites between ad-species on the metal and the oxygen in the oxide. Recent results provide some evidence for another mechanism, in which Pt solely behaves as a promoter to create the most active "$oxide_{red}$/$oxide_{ox}$" interface formed by reduced and oxidized phases in the TMO film.

The results suggest that certain precautions must be taken when using "inverse", i.e. oxide-on-metal, model catalysts to understand reactions occurring on conventional metal/TMO catalysts. It appears that the two-dimensional character

of ultrathin films is important for the structure–reactivity relationships observed.

Finally, well-defined ultrathin TMO films supported on metals may serve as good model systems to examine some aspects of "electron theory of catalysis" which was introduced in the past and based on electron transfer mechanisms.

Compliance with Ethical Standards

Conflict of interest There are no conflicts to declare.

References

1. Tauster SJ, Fung SC, Garten RL (1978) Strong metal-support interactions. Group 8 noble metals supported on titanium dioxide. J Am Chem Soc 100(1):170–175
2. Tauster SJ (1987) Strong metal-support interactions. ACC Chem Res 20(11):389–394
3. Liu J (2011) Advanced electron microscopy of metal–support interactions in supported metal catalysts. ChemCatChem 3(6):934–948
4. Shi XY, Zhang W, Zhang C, Zheng WT, Chen H, Qi JG (2016) Real-space observation of strong metal-support interaction: state-of-the-art and what's the next. J Microsc 262(3):203–215
5. Bernal S, Calvino JJ, Cauqui MA, Gatica JM, Larese C, Pérez Omil JA et al (1999) Some recent results on metal/support interaction effects in NM/CeO$_2$ (NM: noble metal) catalysts. Catal Today 50(2):175–206
6. Qin ZH, Lewandowski M, Sun YN, Shaikhutdinov S, Freund HJ (2008) Encapsulation of Pt nanoparticles as a result of strong metal–support interaction with Fe$_3$O$_4$(111). J Phys Chem C 112(27):10209–10213
7. Haller GL, Resasco DE (1989) Metal–support interaction: group VIII metals and reducible oxides. In: Eley DD, Pines H, Weisz PB (eds) Advances in catalysis, vol 36. Academic Press, San Diego, pp 173–235
8. Bowker M, Stone P, Morrall P, Smith R, Bennett R, Perkins N et al (2005) Model catalyst studies of the strong metal–support interaction: surface structure identified by STM on Pd nanoparticles on TiO2(110). J Catal 234(1):172–181
9. Campbell CT (1997) Ultrathin metal films and particles on oxide surfaces: structural, electronic and chemisorptive properties. Surf Sci Rep 27(1–3):1–111

10. Bauer E (1958) Phänomenologische Theorie der Kristallabscheidung an Oberflächen. I. Z Kristal, p 372

11. Chambers SA (2000) Epitaxial growth and properties of thin film oxides. Surf Sci Rep 39(5):105–180

12. Weiss W, Ranke W (2002) Surface chemistry and catalysis on well-defined epitaxial iron-oxide layers. Prog Surf Sci 70(1–3):1–151

13. Kuhlenbeck H, Shaikhutdinov S, Freund H-J (2013) Well-ordered transition metal oxide layers in model catalysis: a series of case studies. Chem Rev 113(6):3986–4034

14. Franchy R (2000) Growth of thin, crystalline oxide, nitride and oxynitride films on metal and metal alloy surfaces. Surf Sci Rep 38(6–8):195–294

15. Netzer FP, Allegretti F, Surnev S (2010) Low-dimensional oxide nanostructures on metals: hybrid systems with novel properties. J Vac Sci Technol B 28(1):1–16

16. Netzer FP, Fortunelli A (eds) (2016) Oxide materials at the two-dimensional limit. Springer, Cham

17. Wu Q-H, Fortunelli A, Granozzi G (2009) Preparation, characterisation and structure of Ti and Al ultrathin oxide films on metals. Int Rev Phys Chem 28(4):517–576

18. Freund H-J, Pacchioni G (2008) Oxide ultra-thin films on metals: new materials for the design of supported metal catalysts. Chem Soc Rev 37(10):2224–2242

19. Goniakowski J, Finocchi F, Noguera C (2008) Polarity of oxide surfaces and nanostructures. Rep Prog Phys 71(1):016501

20. Willinger MG, Zhang W, Bondarchuk O, Shaikhutdinov S, Freund H-J, Schlögl R (2014) A case of strong metal–support interactions: combining advanced microscopy and model systems to elucidate the atomic structure of interfaces. Angew Chem Int Ed 53(23):5998–6001

21. Vurens GH, Maurice V, Salmeron M, Somorjai GA (1992) Growth, structure and chemical properties of FeO overlayers on Pt(100) and Pt(111). Surf Sci 268(1–3):170–178

22. Dulub O, Hebenstreit W, Diebold U (2000) Imaging cluster surfaces with atomic resolution: the strong metal-support interaction state of Pt supported on TiO$_2$(110). Phys Rev Lett 84(16):3646–3649

23. Barcaro G, Agnoli S, Sedona F, Rizzi GA, Fortunelli A, Granozzi G (2009) Structure of reduced ultrathin TiO$_x$ polar films on Pt(111). J Phys Chem C 113(14):5721–5729

24. Lewandowski M, Sun YN, Qin ZH, Shaikhutdinov S, Freund HJ (2011) Promotional effect of metal encapsulation on reactivity of iron oxide supported Pt catalysts. Appl Catal A 391(1–2):407–410

25. Sun YN, Qin ZH, Lewandowski M, Carrasco E, Sterrer M, Shaikhutdinov S et al (2009) Monolayer iron oxide film on platinum promotes low temperature CO oxidation. J Catal 266(2):359–368

26. Sun Y-N, Giordano L, Goniakowski J, Lewandowski M, Qin Z-H, Noguera C et al (2010) The interplay between structure and CO oxidation catalysis on metal-supported ultrathin oxide films. Angew Chem Int Ed 49(26):4418–4421

27. Giordano L, Lewandowski M, Groot IMN, Sun YN, Goniakowski J, Noguera C et al (2010) Oxygen-induced transformations of an FeO(111) film on Pt(111): a combined DFT and STM study. J Phys Chem C 114(49):21504–21509

28. Martynova Y, Shaikhutdinov S, Freund H-J (2013) CO oxidation on metal-supported ultrathin oxide films. What makes them active? ChemCatChem 5(8):2162–2166

29. Weng X, Zhang K, Pan Q, Martynova Y, Shaikhutdinov S, Freund H-J (2017) Support effects on CO oxidation on metal-supported ultrathin FeO(111) films. ChemCatChem 9(4):705–712

30. Boffa AB, Lin C, Bell AT, Somorjai GA (1994) Lewis acidity as an explanation for oxide promotion of metals: implications of its importance and limits for catalytic reactions. Catal Lett 27(3–4):243–249

31. Gunter PLJ, Niemantsverdriet JW, Ribeiro FH, Somorjai GA (1997) Surface science approach to modeling supported catalysts. Catal Rev 39(1–2):77–168

32. Hayek K, Fuchs M, Klötzer B, Reichl W, Rupprechter G (2000) Studies of metal–support interactions with "real" and "inverted" model systems: reactions of CO and small hydrocarbons with hydrogen on noble metals in contact with oxides. Top Catal 13(1):55–66

33. Leisenberger FP, Surnev S, Koller G, Ramsey MG, Netzer FP (2000) Probing the metal sites of a vanadium oxide–Pd(111) 'inverse catalyst': adsorption of CO. Surf Sci 444(1):211–220

34. Fu Q, Li W-X, Yao Y, Liu H, Su H-Y, Ma D et al (2010) Interface-confined ferrous centers for catalytic oxidation. Science 328(5982):1141–1144

35. Sun D, Gu X-K, Ouyang R, Su H-Y, Fu Q, Bao X et al (2012) Theoretical study of the role of a metal–cation ensemble at the oxide–metal boundary on CO oxidation. J Phys Chem C 116(13):7491–7498

36. Pan Q, Weng X, Chen M, Giordano L, Pacchioni G, Noguera C et al (2015) Enhanced CO oxidation on the oxide/metal interface: from ultra-high vacuum to near-atmospheric pressures. ChemCatChem 7(17):2620–2627

37. Fu Q, Yao Y, Guo X, Wei M, Ning Y, Liu H et al (2013) Reversible structural transformation of FeO$_x$ nanostructures on Pt under cycling redox conditions and its effect on oxidation catalysis. Phys Chem Chem Phys 15(35):14708–14714

38. Zhang K, Li L, Shaikhutdinov S, Freund H-J (2018) Carbon monoxide oxidation on metal-supported monolayer oxide films: establishing which interface is active. Angew Chem Int Ed 57(5):1261–1265

39. Lewandowski M, Groot IMN, Shaikhutdinov S, Freund HJ (2012) Scanning tunneling microscopy evidence for the Mars-van Krevelen type mechanism of low temperature CO oxidation on an FeO(111) film on Pt(111). Catal Today 181(1):52–55

40. Walton AS, Fester J, Bajdich M, Arman MA, Osiecki J, Knudsen J et al (2015) Interface controlled oxidation states in layered cobalt oxide nanoislands on gold. ACS Nano 9(3):2445–2453

41. Fester J, García-Melchor M, Walton AS, Bajdich M, Li Z, Lammich L et al (2017) Edge reactivity and water-assisted dissociation on cobalt oxide nanoislands. Nat Commun 8:14169

42. Fester J, Sun Z, Rodríguez-Fernández J, Walton A, Lauritsen JV (2018) Phase transitions of cobalt oxide bilayers on Au(111) and Pt(111): the role of edge sites and substrate interactions. J Phys Chem B 122(2):561–571

43. Janotti A, Walle CGVd (2005) Oxygen vacancies in ZnO. Appl Phys Lett 87(12):122102

44. Martynova Y, Liu BH, McBriarty ME, Groot IMN, Bedzyk MJ, Shaikhutdinov S et al (2013) CO oxidation over ZnO films on Pt(111) at near-atmospheric pressures. J Catal 301(0):227–232

45. Pan Q, Liu BH, McBriarty ME, Martynova Y, Groot IMN, Wang S et al (2014) Reactivity of ultra-thin ZnO films supported by Ag(111) and Cu(111): a comparison to ZnO/Pt(111). Catal Lett 144(4):648–655

46. Liu X, Korotkikh O, Farrauto R (2002) Selective catalytic oxidation of CO in H$_2$: structural study of Fe oxide-promoted Pt/alumina catalyst. Appl Catal A 226(1):293–303

47. Shaikhutdinov S, Freund H-J (2012) Ultrathin oxide films on metal supports: structure-reactivity relations. Annu Rev Phys Chem 63(1):619–633

48. Over H (2012) Surface chemistry of ruthenium dioxide in heterogeneous catalysis and electrocatalysis: from fundamental to applied research. Chem Rev 12(6):3356–3426

49. Pankratiev YD (1982) Correlation between oxygen binding energy and catalytic activity of oxides. React Kinet Catal Lett 20(3):255–259

50. Vol'kenshtein FF (1966) Experiment and the electronic theory of catalysis. Russ Chem Rev 35(7):537
51. Schwab G-M (1979) Electronics of supported catalysts. In: Eley DD, Pines H, Weisz P (eds) Advances in catalysis, Vol 27. Academic Press, San Diego, pp 1–22
52. Sterrer M, Risse T, Martinez U, Giordano L, Heyde M, Rust H-P et al (2007) Control of the charge state of metal atoms on thin MgO films. Phys Rev Lett 98(9):096107
53. Giordano L, Pacchioni G (2011) Oxide films at the nanoscale: new structures, new functions, and new materials. Acc Chem Res 44(11):1244–1252
54. Grönbeck H (2006) Mechanism for NO_2 charging on metal supported MgO. J Phys Chem B 110(24):11977–11981
55. Gonchar A, Risse T, Freund H-J, Giordano L, Di Valentin C, Pacchioni G (2011) Activation of oxygen on MgO: O_2.—radical ion formation on thin, metal-supported MgO(001) films. Angew Chem Int Ed 50(11):2635–2638
56. Merte LR, Heard CJ, Zhang F, Choi J, Shipilin M, Gustafson J et al (2016) Tuning the reactivity of ultrathin oxides: NO adsorption on monolayer FeO(111). Angew Chem Int Ed 55(32):9267–9271
57. Hellman A, Klacar S, Grönbeck H (2009) Low temperature CO oxidation over supported ultrathin MgO films. J Am Chem Soc 131(46):16636–16637