Catalysis with thin films

Interplay between structure and CO oxidation catalysis on metal supported ultrathin oxide films**

Ying-Na Sun, Livia Giordano, Jacek Goniakowski, Mikolaj Lewandowski, Zhi-Hui Qin, Claudine Noguera, Shamil Shaikhutdinov, Gianfranco Pacchioni*, Hans-Joachim Freund*

Thin oxide films grown on metal single crystal substrates have been successfully used as suitable supports to model disperse metal catalysts.[1-9] This is even true for ultrathin films (2 - 5 oxide layers), depending on the specific system. However, in those cases the supporting metal may, in favorable cases, determine the properties of adsorbates and hence its reactivity.[10, 11] Basically, similar ideas have been around since the late 40-s of the last century, when Cabrera and Mott explained the growth of passivation (oxide) layers on Cu by assuming the formation of peroxo species responsible for the growth of the oxide layer.[12] Vol'kenshtein in Russia[13] developed ideas along similar lines for catalysis based on the then ´en vogue´ concept of Schottky barriers. According to those concepts semiconductor films on metals could be utilized to control electron transfer to surface bound species rendering them catalytically active. A citation from Vol'kenshtein's review paper in 1966 underlines this: "The semiconductor film arises as a result of oxidation of a metal, and its thickness can often be controlled to some extend … By varying the thickness … it is possible to control the adsorption capacity, the catalytic activity, and the selectivity … It would be interesting to study the adsorption and catalytic properties of a semiconducting film on a metal, and their changes, during growth of the film." This citation speaks for itself! In the 60-s, when Vol'kenshtein mentioned this in his review,[13] the experimental tools were not available to study this question properly, as characterization of ultrathin-film systems was not possible at the atomic level. The ideas faded away and researchers did not pay attention. Also, in the late 70-s, when the so called "Strong Metal Support Interaction (SMSI)"[14-16] was introduced, thin oxide films, migrating from a reducible oxide onto metal particles supported there upon, were shown to suppress the reactivity of the system, instead of increasing its reactivity. There have been attempts to study t he influence of the thickness of thin metal film catalysts.[17, 18] Only recently it was experimentally observed that thin oxide films

on metals, indeed, may exhibit greatly enhanced catalytic activity[19], i.e. higher than the metal substrate underneath under the same conditions. The example studied was CO oxidation on a FeO(111) film grown on a Pt(111) single crystal at a temperature when Pt is inactive. It was suggested that under reaction conditions at oxygen partial pressure in the mbar range, the bi-layer FeO film restructures leading to a tri-layer OFeO film which exhibits the observed reactivity. In this paper we present both, experimental evidences for the structure/morphology of the active film, and theoretical modeling that reveals the mechanism of its formation and the observed CO oxidation on its surface. We will discuss the results in light of the Mott-Cabrera- Vol'kenshtein work as well as the recently observed charging of adsorbed species - metal atoms, clusters, and molecules - on metal-supported ultrathin oxide films.[20, 21]

The atomic structure of FeO(111) film on Pt(111) has been explored in details (e.g., see[8, 22-24]). The film consists of two close-
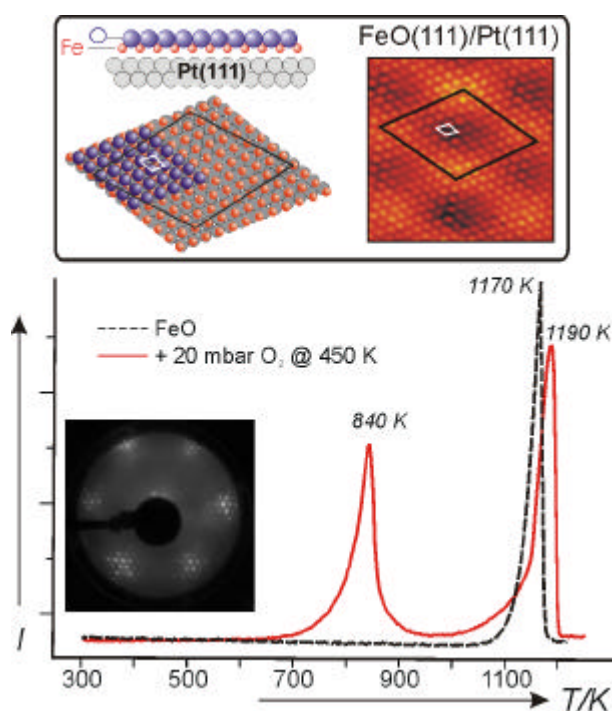
Figure 1. (Top) Cross and top views of a FeO(111) film on Pt(111). Not all O atoms are shown in the top view, for clarity. Unit cells of FeO and Moiré superstructure are also indicated in the high-resolution STM image, (size 6 nm x 6 nm). (Bottom) Thermal desorption spectra of a pristine FeO(111) film (dashed line) and an O-rich film (solid line) produced by exposure to 20 mbar of O_2 at 450 K (32 amu (O_2) signal is shown). The inset shows a LEED pattern of an O-rich film with floreted diffraction spots c haracteristic of the Moiré superstructure.

[∗] M. Lewandowski, Dr. Z.-H. Qin, Dr. S. Shaikhutdinov, Prof. H.-J. Freund
Abteilung Chemische Physik
Fritz-Haber Institut der Max-Planck Gesellschaft
Faradayweg 4-6, 14195 Berlin, Germany
Fax: (+49) 30 8413 4101
E-Mail: shaikhutdinov@fhi-berlin.mpg.de

Dr. L. Giordano, Prof. G. Pacchioni
Dipartimento di Scienza dei Materiali
Università di Milano-Bicocca
via Cozzi 53, 20125 Milano, Italy
E-mail: gianfranco.pacchioni@unimib.it

Dr. J. Goniakowski, Prof. C. Noguera
Institut des Nanosciences de Paris
CNRS UMR 7588 and UPMC Université
Paris 06, 140 rue de Lourmel, 75015 Paris, France

surface exhibits the Moiré superstructure with a ~26 Å periodicity which is clearly observed in high-resolution scanning tunneling microscopy (STM) images.

At low pressures up to 10^{-3} mbar (at 300 K) the film is essentially inert towards CO and O_2. The film restructures upon increasing O_2 pressure: It becomes enriched in oxygen and approaches the formal stoichiometry FeO_x (x ~ 1.8 – 1.9) upon exposure to 20 mbar O_2 at 450 K as measured by Auger electron spectroscopy (AES). The oxygen enrichment in these films (thereafter referred to as O-rich) is further evidenced by thermal desorption spectroscopy (TDS). Pristine FeO films show a single O_2 desorption peak at ~1170 K as a result of the film decomposition (see Fig. 1). In addition, O-rich films exhibit desorption at 840 K, clearly showing that the O-rich film possesses two energetically different O species. The integral intensity of the low-temperature peak is 80-90 % of the high-temperature peak, on average, which is in turn almost equal in intensity to that measured on pristine films. This finding is in full agreement with ~90 % enrichment observed by AES

The O-rich film maintains long-range ordering since the corresponding low energy electron diffraction (LEED) pattern is almost identical to that of the FeO(111)/Pt(111) surface (Fig. 1). The superstructure is clearly seen in STM images of the film exposed to 20 mbar of O_2 at 450 K for 10 min (Fig. 2a). The profile line presented in Fig. 2c reveals height modulation about 0.6 Å in amplitude (independent of the bias polarity), i.e., much higher than ~0.1 Å observed on the pristine FeO films under the same tunneling conditions.
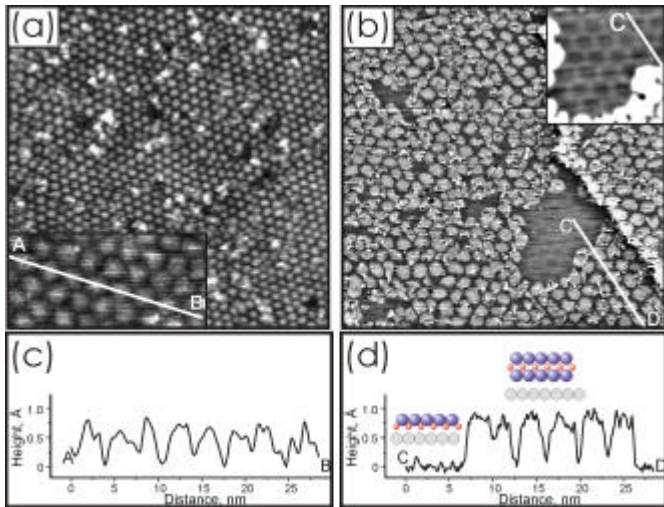
Figure 2. STM images and profile lines of the FeO films exposed to 20 mbar O_2 at 450 K for 10 min (a, c) and 2 mbar O_2 at 300 K for 5 hours (b, d). The insets show close-ups of the corresponding surfaces. The Moiré superstructure of the pristine FeO film is seen in the inset (b). Image sizes are 100 nm x 100 nm (a) and 50 nm x 50 nm (b); tunneling bias and current are 1 V, 0.7 nA (a) and 0.25 V, 0.3 nA (b).

Figure 2b shows the STM image of a FeO film exposed to 2 mbar O_2 at 300 K. This treatment resulted in partial surface restructuring such that pristine and reconstructed surfaces coexist, indicating that the phase diagram of the FeO film indeed strongly depends on the oxygen chemical potential. The presence of both structures allowed us to measure the height difference between them, i.e., ~0.65 Å, which basically coincides with a Fe-O interlayer distance on FeO(111)/Pt(111).[22] This finding is fully consistent

with the formation of additional O-layer upon film restructuring as schematically shown in Fig. 2d.

Figure 2b also revealed that reconstructed areas, at least under mild conditions (2 mbar O_2, 300 K), exhibit irregularly shaped, flat islands apparently decorating the Moiré "template" of FeO. Based on the profile line shown in Fig. 2d the surface between the islands exposes unreconstructed, bi-layer FeO(111). Such morphology can be rationalized in terms of different reactivity of domains within the Moiré cell towards oxygen as previously observed for interaction of ad-species with FeO(111)/Pt(111).[25, 26] Apparently, increasing temperature and pressure renders reconstruction more facile and homogeneous as shown in Fig. 2a, where the protrusions appear hemispherical and uniform across the whole surface. However, the corrugation amplitude (i.e., ~0.6 Å as shown in Fig. 2c) is close to the height of "isolated" islands in Fig. 2b. Therefore, one cannot exclude the presence of regular defects in the ideal tri-layer film, arising, for example, upon lateral growth of reconstructed islands. Another explanation for the observed morphology involves much stronger rumpling of the O- and Fe-layers within the tri-layer structure as compared to the bi-layer structure, which could result in high surface corrugation as observed in STM.

From a modeling point of view we first investigated on the DFT level the possibilities to describe the transformation of the FeO bi-layer under exposure to oxygen into a FeO_2 tri-layer. We have found that the energetics of this transformation is strongly dependent on the registry between the oxide and the metal, as suggested above by STM, and is the most favorable in the O-top region of the Moiré structure. Thus, in the following we focus on the results obtained for this registry, using both, a pseudomorphic and a non-pseudomorphic, models[27] (see Experimental Section).

Figure 3 shows the calculated enthalpy profile for interaction of O_2 with the FeO/Pt(111) film. By overcoming a small energy barrier (0.3 eV) O_2 chemisorbs molecularly with adsorption energy of 0.7 eV on the Fe atom, which is pulled out from the pristine film. The presence of a small barrier to reach the chemisorbed state implies that an oxygen pressure is necessary, since thermal activation would result in O_2 desorption. In the chemisorbed state electrons are transferred from the oxide/metal substrate, and adsorbed O_2 becomes negatively charged. The O-O bond length expands to 1.46 Å, and the magnetic moment is fully quenched, indicating the formation of O_2^{2-} peroxo species. Such an electron transfer is enabled mainly by a local inversion of the rumpling in the oxide film which lowers locally the work function of the support (?F ~ -1.5 eV), similar to transition metal ad-atoms on metal-supported oxide films.[20]

The activated O_2 is a precursor of a dissociative path: a second activation barrier of about 0.4 eV separates it from the final product of the reaction, corresponding to two O ad-atoms (Fig. 3a). This shows that O_2 dissociation on FeO/Pt is a relatively easy process which can occur under O_2 pressure at mild temperatures. At high O_2 coverage, the interaction results in the formation of a O-Fe-O tri-layer structure with FeO_2 stoichiometry, with a total energy gain of 3 eV.

Having found that a FeO_2 tri-layer may be formed relatively easily under oxygen pressure, it is near at hand that a direct reaction of CO with the surface oxygen should be feasible. This step has thus been investigated by computing the enthalpy profile of the reaction $CO + FeO_2/Pt(111) \rightarrow CO_2 + FeO_{2-x}/Pt(111)$, Figure 3(b). The reaction involves the extraction of an oxygen atom from the oxide film with formation of a CO_2 molecule leaving behind an oxygen vacancy.
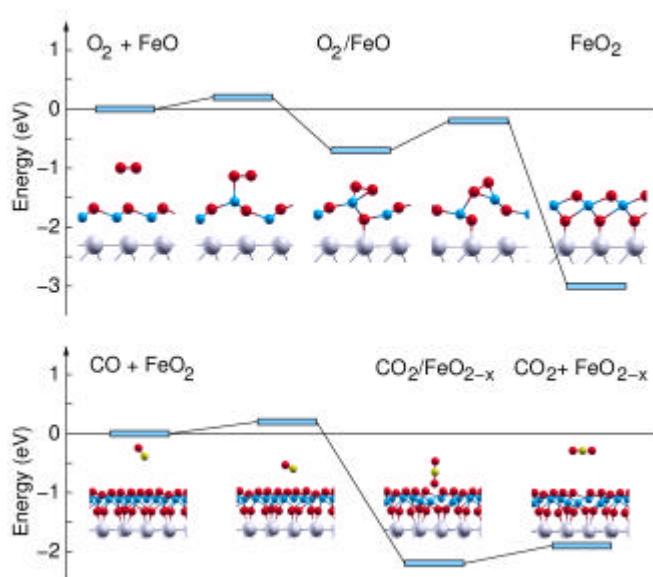
Figure 3. (top) Energy profile for the oxidation of the FeO/Pt(111) film upon exposure to O_2 at high oxygen coverage. (bottom) Energy profile for CO oxidation on FeO_2/Pt(111) film at low CO coverage. Blue (Fe), red (O), yellow (C), gray (Pt).

A CO molecule located near the FeO_2/Pt(111) substrate is, at most, physisorbed. A reaction occurs by overcoming a barrier of ~ 0.2 eV (Fig. 3b), which is considerably lower than the computed barrier on Pt(111), of the order of 1 eV.[28] The CO molecule binds strongly with the C-end to one O ion in the topmost layer, with formation of a stable CO_2 molecule and an oxygen vacancy. The cost for CO_2 desorption is 0.3 eV only. Because of the low activation energy the reaction may indeed occur at lower temperatures than typically used for Pt catalysts as experimentally observed.[19] Note that, in our model, only the reaction at the flat terraces of the FeO_2/Pt(111) film has been considered. It is likely that CO interaction at the border of FeO_2 islands revealed by STM (Fig. 2) can occur with a lower energy cost, making the reaction easier.

The formation of a strong C-O bond in CO_2 overcompensates the cost of removing an O atom such that the overall reaction is highly exothermic, with a computed enthalpy of -1.9 eV. This is due to the relatively low formation energy of an oxygen vacancy on the FeO_2/Pt(111) surface, *i.e.*, 1.3 eV, with respect to ½ O_2, about one half of that calculated for the pristine FeO film (2.8 eV). The latter finding is in full agreement with TDS results shown in Fig. 1, where oxygen desorbs from FeO-rich films at much lower temperature than from FeO (840 K vs 1170 K). Therefore, the formation energy of an oxygen vacancy is the key factor in the CO oxidation reaction over FeO films.

To end the catalytic cicle via the Mars-van Krevelen type mechanism the oxygen vacancies must be replenished through the reaction with gas-phase oxygen that restores the original stoichiometry of the film. This part of the reaction can occur in regions where the oxygen depletion leads locally to areas covered by FeO instead of FeO_2 films. In this case, the oxygen dissociation process basically follows the mechanism described in previous section.

The scenario proposed above should be discussed with respect to the recently observed transfer of charge through ultrathin oxide films of alumina and magnesia, for which the phenomenon, mentioned in the Introduction, has been studied both, theoretically

and experimentally (see [10] and references therein). It has been proposed that O_2 molecules adsorbed on 2-3 MgO layers supported on Ag(100) transform spontaneously into superoxide anions, O_2^-, by the tunneling mechanism described above, which promotes low-temperature CO oxidation.[28] The reason is the relatively low work function for this system. Conversely, FeO/Pt(111) films exhibit a very high work function, mainly determined by the Pt(111) surface, which makes electron transfer from the metal/oxide interface to the adsorbate unlikely as previously demonstrated for Au ad-atoms. [21,27] However, due to the local restructuring of the film upon exposure to oxygen, the work-function is locally lowered, leading to the transient formation of a peroxo species.

Experimental Section

The experiments were performed in ultra-high vacuum chamber equipped with LEED, AES, STM, and a mass spectrometer for TDS experiments (see ref. 19 for details). FeO(111) films were prepared by deposition of one monolayer of Fe (99.95%) onto clean Pt(111) at 300 K and annealing in 10^{-6} mbar O_2 at 1000 K for 2 min. For "high-pressure" treatments performed in the Au-plated reactor, O_2 (99.999%) was additionally cleaned using a cold trap kept at ~ 200 K.

The calculations are based on the DFT+U approach[29] ($U_{Fe} - J_{Fe} = 3$ eV) using the Perdew-Wang 91 functional,[30] as implemented in the VASP code.[31, 32] We used two different interface models[27], a (2x1) pseudomorphic structure for each of the high symmetry regions of the Moiré cell (Fe-top, -fcc, and -hcp), and a non-pseudomorphic model, obtained by superposition of (v7xv7)R19°-FeO(111) and (3x3)-Pt(111) structures. The two models represent high and low O_2 coverage, respectively. Reaction profiles have been studied by means of the climbing image nudged elastic band method.[33]

[1] H.-J. Freund, D. W. Goodman, in *Handbook of Heterogeneous Catalysis*, 2. ed. (Eds.: G. Ertl, H. Knözinger, F. Schüth, J. Weitkamp), Wiley-VCH Verlagsgesellschaft mbH, Weinheim, **2007**, pp. 1309-1338.

[2] G. Ertl, H.-J. Freund, *Phys. Today* **1999**, *52*, 32.

[3] D. W. Goodman, *Surf. Rev. Lett.* **1995**, *2*, 9.

[4] C. T. Campbell, *Surf. Sci. Rep.* **1997**, *27*, 1.

[5] H.-J. Freund, *Angew. Chem. Int. Ed.* **1997**, *36*, 452.

[6] C. R. Henry, *Surf. Sci. Rep.* **1998**, *31*, 231.

[7] H.-J. Freund, *Surf. Sci.* **2002**, *500*, 271.

[8] W. Weiss, W. Ranke, *Progr. Surf. Sci.* **2002**, *70*, 1.

[9] M. Bäumer, H.-J. Freund, *Progr. Surf. Sci.* **1999**, *61*, 127.

[10] H.-J. Freund, G. Pacchioni, *Chem. Soc. Rev.* **2008**, *37*, 2224.

[11] N. Nilius, *Surf. Sci. Rep.* **2009**, *64*, 595.

[12] N. Cabrera, N. F. Mott, *Rep. Progr. Phys.* **1948**, *12*, 163.

[13] F. F. Vol'kenshtein, *Russ. Chem. Rev.* **1966**, *35*, 537.

[14] S. J. Tauster, S. C. Fung, R. L. Garten, *J. Am. Chem. Soc.* **1978**, *100*, 170.

[15] E. I. Ko, R. L. Garten, *J. Catal.* **1981**, *68*, 233.

[16] G. L. Haller, D. E. Resasco, *Adv. Catal.* **1989**, *36*, 173.

[17] A. B. McEwen, W. F. Maier, R. H. Fleming, S. M. Baumann, *Nature* **1987**, *329*, 531.

[18] J. M. Cogen, K. Ezaz-Nikpay, R. H. Fleming, S. M. Baumann, W. F. Maier, *Angew. Chem. Int. Ed.* **1987**, *26*, 1182.

[19] Y.-N. Sun, Z.-H. Qin, M. Lewandowski, E. Carrasco, M. Sterrer, S. Shaikhutdinov, H.-J. Freund, *J. Catal.* **2009**, *266*, 359.

[20] J. Goniakowski, C. Noguera, L. Giordano, G. Pacchioni, *Phys. Rev. B* **2009**, *80*, 125403.

[21] L. Giordano, G. Pacchioni, J. Goniakowski, N. Nilius, E. D. L. Rienks, H.-J. Freund, *Phys. Rev. Lett.* **2008**, *101*, 026102.

[22] Y. J. Kim, C. Westphal, R. X. Ynzunza, H. C. Galloway, M. Salmeron, M. A. Van Hove, C. S. Fadley, *Phys. Rev. B* **1997**, *55*, R13448.

[23] G. H. Vurens, M. Salmeron, G. A. Somorjai, *Surf. Sci.* **1988**, *201*, 129.

[24] M. Ritter, W. Ranke, W. Weiss, *Phys. Rev. B* **1998**, *57*, 7240.

[25] N. Nilius, E. D. L. Rienks, H.-P. Rust, H.-J. Freund, *Phys. Rev. Lett.* **2005**, *95*, 066101.

[26] J. Knudsen, L. R. Merte, L. C. Grabow, F. M. Eichhorn, S. Porsgaard, H. Zeuthen, R. T. Vang, E. Lægsgaard, M. Mavrikakis, F. Besenbacher, *Surf. Sci.* **2009**, *604*, 11.

[27] L. Giordano, G. Pacchioni, J. Goniakowski, N. Nilius, E. D. L. Rienks, H.-J. Freund, *Phys. Rev. B* **2007**, *76*, 075416.

[28] A. Hellman, S. Klacar, H. Grönbeck, *J. Am. Chem. Soc.* **2009**, *131*, 16636.

[29] S. L. Dudarev, G. A. Botton, S. Y. Savrasov, C. J. Humphreys, A. P. Sutton, *Phys. Rev. B* **1998**, *57*, 1505.

[30] J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, C. Fiolhais, *Phys. Rev. B* **1992**, *46*, 6671.

[31] G. Kresse, J. Hafner, *Phys. Rev. B* **1993**, *47*, 558.

[32] G. Kresse, J. Furthmüller, *Phys. Rev. B* **1996**, *54*, 11169.

[33] G. Henkelman, B. P. Uberuaga, H. Jonsson, *J. Chem. Phys.* **2000**, *113*, 9901.

Oxide film thickness matters

Y.-N. Sun, L. Giordano, J. Goniakowski,
M. Lewandowski, Z.-H. Qin, C. Noguera,
S. Shaikhutdinov*, G. Pacchioni*, H.-J.
Freund

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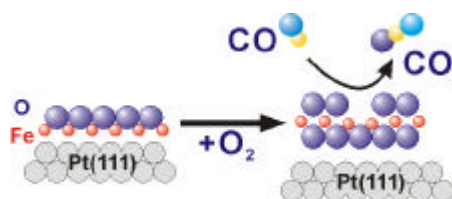
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