Activation of Oxygen on MgO: $O_2^{·-}$ Radical Ion Formation on Thin, Metal-Supported MgO(001) Films**

Anastasia Gonchar, Thomas Risse, Hans-Joachim Freund, Livia Giordano, Cristiana Di Valentin, and Gianfranco Pacchioni*

Dedicated to Professor Elio Giamello on the occasion of his 60th birthday

Thermodynamically stable, fully stoichiometric surfaces of simple oxides such as MgO(100), are generally believed to be inactive with respect to chemical reactions. Defects are thought to control the chemistry occurring on such surfaces.[1] While this perception is certainly true for bulk oxides this may or may not hold if the oxide surface is in close proximity to a metal as it is found for example in supported ultrathin films. The idea that the supporting metal may influence the properties of adsorbates and thus their reactivity can be traced back to the model of Cabrera and Mott[2] from the late 1940s explaining the growth of passivating (oxide) layers on Cu and ideas developed by Vol'kenshtein[3] who pointed out a few decades ago that the chemical properties of the oxide might be altered significantly if used as a thin film of a few monolayer in thickness. This subject has recently found resurgence by theoretical calculations predicting altered properties for metal deposits as well as molecular adsorbates.[4,5] In particular, it was predicted that metals with a rather high electron affinity, such as gold, will become negatively charged when adsorbed on thin oxide films with a rather low work function, such as MgO grown on Mo or Ag. By now there is experimental verification for this prediction.[6,7]

More importantly, it was recently shown that a thin FeO(111) film grown on Pt(111) has unexpected catalytic properties for CO oxidation.[8] The theoretical analysis has shown that activated molecular oxygen species are important for the understanding of the mechanism of this reaction.

Interestingly, theory has also shown that activated molecular oxygen—namely $O_2^{·-}$ radical ions—should form spontaneously on thin, metal-supported MgO films.[9,10] While the oxygen radical is found to be a stable intermediate on MgO, where it is centered above two adjacent Mg^{2+} ions of the surface (Figure 1), it is only a transient species on the FeO film. The stability of the $O_2^{·-}$ radical ion on the MgO surface (1.5 eV and 0.6–0.8 eV for MgO films on Mo and Ag, respectively) should allow for a spectroscopic characterization of this species. However, this stability makes the investigation of catalytic oxidation processes more demanding than in case of FeO.[9]

The aim of this study is to provide experimental evidence for the formation of $O_2^{·-}$ radicals and thus provide support for

[*] A. Gonchar, Prof. Dr. T. Risse,[+] Prof. Dr. H.-J. Freund
Fritz Haber Institute of the Max Planck Society
Department of Chemical Physics
Faradayweg 4-6, 14195, Berlin (Germany)
Fax: (+49) 30-8413-4316
E-mail: risse@chemie.fu-berlin.de

Dr. L. Giordano, Dr. C. Di Valentin, Prof. Dr. G. Pacchioni
Dipartimento di Scienza dei Materiali, Università di Milano-Bicocca
via R. Cozzi, 53, I-20125 Milano (Italy)

[+] Permanent address: Freie Universität Berlin
Institute of Chemistry and Biochemistry
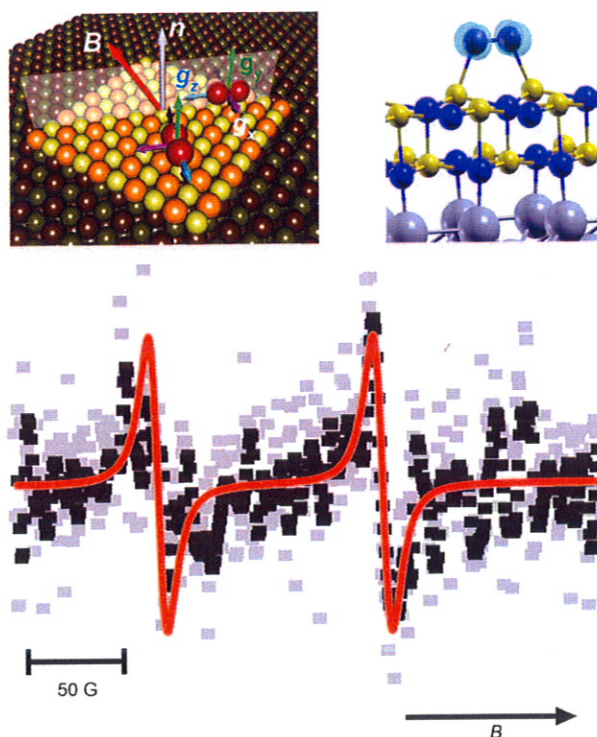Takustr.3, 14195 Berlin (Germany)

Figure 1. Top left: oxygen molecules (red) adsorbed on 2 ML MgO films (yellow/orange) as predicted by theory together with the orientation of the magnetic field as used in the experiment; top right: result of a DFT calculation of O_2 on a 2 ML thin MgO(001) film on Mo(001) showing the polaronic distortion of the MgO lattice (Mg yellow, O blue). Bottom: EPR spectrum of 20 Langmuir O_2 adsorbed at 40 K on a 4 ML thick MgO(001) film on Mo(001) with the magnetic field oriented in the surface plane.

the mechanism put forward by theory. EPR spectroscopy is well suited to address this question as it has the required sensitivity to detect radicals in submonolayer quantities. On single-crystal surfaces the angle between the magnetic field and surface crystallographic directions may be chosen which allows the orientation of the molecule and the corresponding g-tensor of the molecules to be determined. As the electronic structure of the molecule correlates with the g-tensor the experimental results will be compared to theoretical calculations to gain additional insight into the properties of the adsorbed radicals.

The EPR experiments were performed under ultrahigh vacuum on single-crystalline MgO(001) films grown in situ on a Mo(001) single crystal. Figure 1 shows an EPR spectrum obtained after adsorbing 20 L (1 Langmuir is 10^{-6} Torr s) molecular oxygen at 40 K on a 4 monolayer (ML) thick MgO(001) film. The magnetic field was oriented in the surface plane along what is equivalent to the [110] direction. The spectrum consists of two lines localized at g-values of 2.072 and 2.002. The signal positions are in line with those reported for $O_2^{\cdot-}$ radical species on chemically modified MgO, for which two g-tensors (g_{xx}, g_{yy}) components were found at around 2.0023 and 2.007 while the third one (g_{zz}) varies between 2.062–2.091 for different surface sites.[11–13] This signal is only observed for thin MgO films. Increasing the film thickness to 8 ML results in a reduction of the signal intensity by 50 % and above 15 ML no signal is found. For films of 4 ML thickness this signal corresponds to 0.02–0.05 monolayer of $O_2^{\cdot-}$ based on the number of Mg cations on the ideal MgO(001) surface. Heating of the sample up to 350 K did not alter the EPR spectrum taken at 40 K. This result is consistent with the theoretically expected adsorption energy of 1.5 eV arising from the polaronic distortion of the lattice (Figure 1, top right).

Figure 1 shows the adsorption geometry as predicted by theory. It is seen that the molecules are expected to be oriented with their main axis along the [110] direction of the MgO(001) surface. Owing to the fourfold symmetry of the surface, two classes of magnetically inequivalent molecules are expected. Half of the molecules are aligned along the magnetic field while the other half are rotated by 90° leading to a perpendicular orientation of the molecule and the magnetic field. As the orientation of the g-tensor has to fulfill the symmetry requirements imposed by the adsorption sites, it is evident that one of the tensor components is parallel to the long axis of the molecule, one is pointing perpendicular to the surface and the third one is orthogonal to these two. For $O_2^{\cdot-}$ radicals the three directions are labeled z, y, and x, respectively. If the theoretically predicted adsorption geometry is correct, the spectrum shown in Figure 1 would allow to determine the z and x component of the g-tensor directly as indicated in Figure 1. However, two-line spectra are expected under the given experimental conditions for a variety of other adsorption geometries as well. As a result, it is not possible from this experiment alone to deduce the orientation of the molecule. To demonstrate the azimuthal orientation of the molecule an additional experiment is required. Given the symmetry of the surface it is readily seen from Figure 1 that a rotation of the magnetic field in the surface by 45° (along a

[100] equivalent direction) would render the two molecules indistinguishable by means of EPR spectroscopy. Thus, a single line would be expected in the EPR spectrum. The lowest trace in Figure 2 shows the corresponding spectrum.
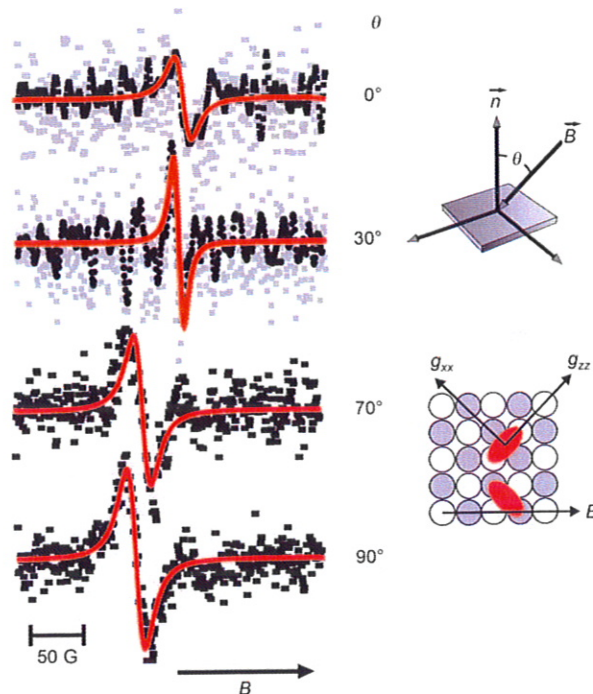

Figure 2. EPR spectra taken for 20 Langmuir O_2 adsorbed at 30 K on a 4 ML thick MgO(001) film grown on Mo(001) as a function of the polar angle θ. The magnetic field was oriented in a plane spanned by a direction equivalent to [100] in the surface and the surface normal. Top right: definition of the angle θ. Bottom right: top view of the adsorption geometry (O_2 ovals).

Indeed only a single line is observed which is located at $g = 2.0037$ as expected from the considerations above. In addition to the spectrum taken with the magnetic field oriented in the surface plane, also, angular-dependent spectra for different polar angles are reported in Figure 2. The angular dependence reveals a simple $\cos^2$ dependence with the extreme values found at 90° and 0°, respectively. This result allows us to determine the orientation of the tensor. Two tensor components are oriented in the surface plane and the two orthogonal components are aligned to [110] equivalent directions. The third component is oriented perpendicular to the surface. This result is exactly in line with the expectation based on theory. Correspondingly, the value of the g-tensor components can be deduced from the spectrum in Figure 1 and the topmost spectrum in Figure 2 if the absolute field values and the corresponding microwave frequencies are known to be $g_{xx} = 2.002$, $g_{yy} = 2.012$, $g_{zz} = 2.072$. These results allow us to conclude that molecular oxygen adsorbed on ultrathin MgO films below about 8 ML thickness becomes activated by an electron transfer from the substrate to form $O_2^{\cdot-}$ radicals which represents the first direct experimental verification of such oxygen activation on a stoichiometric low-energy oxide surface.

It is instructive to compare the g-tensor components measured in this case to values found for $O_2^{\cdot-}$ radicals on the terraces of MgO powders, which were prepared and activated by chemical means.[14] The g-tensor components are given in Table 1, the x component is unchanged, the y component of

Table 1: Measured and computed g-tensor for $O_2^{\cdot-}$ adsorbed on the surface of MgO/Mo(001) films and MgO powders.

Surface	Site	g_{xx}	g_{yy}	g_{zz}	$d(O-Mg)$ [Å]	$d(O-O)$ [Å]
MgO/Mo(001) exp. (this work)	Terrace	2.002	2.012	2.072	–	–
MgO powders exp.[12]	Terrace	2.002	2.008	2.091	–	–
MgO powders exp.[11]	Edge	2.002	2.008	2.077	–	–
MgO(001) theory[14][a]	Terrace	2.0022	2.0092	2.0639	2.329	1.345
MgO(001) theory[14][a]	Edge	2.0021	2.0096	2.0527	2.158	1.353
MgO(001) with polaronic distortion theory (this work)	Terrace	2.0025	2.0093	2.0560	2.075	1.345

[a] Notice that in Ref. [14] a different sign convention is adopted for the orientation of the axes.

the tensor is slightly decreased while a significantly larger z component is found on powders. Understanding these differences requires a detailed understanding of the electronic structure, which we have addressed by theory. To investigate these differences a calculation of the g-tensor was performed for an $O_2^{\cdot-}$ radical adsorbed on a pure MgO cluster model representing a (001) surface. The calculated g-tensor components as well as the geometry, which was obtained after optimizing this model, are shown in Table 1. As expected for charged molecules, the oxygen bond length is elongated compared to the neutral molecule. When comparing the calculation to the measurement on the powder it is readily seen that the x component of the tensor is well reproduced, the y component is also well reproduced, while the z component is considerably underestimated. Detailed studies have shown that the g_{zz} component is systematically underestimated in all calculations of $O_2^{\cdot-}$ species.[14] However, trends, for example, found when comparing the $O_2^{\cdot-}$ radicals adsorbed on terrace and edge Mg^{2+} sites of MgO, which reveal a reduction of the z component with decreasing coordination number, are well reproduced by theory (see Ref. [14] and Table 1).

What are the implications of this finding for the thin film situation? The model used so far describes the situation as found on the powdered material where the main stabilization effect of the thin film, namely the polaronic distortion of the lattice, is absent. A calculation forcing the MgO cluster model into the polaronically distorted geometry found for a supported thin oxide film (obtained by a periodic DFT calculation), indeed, reveals a sizable reduction of the g_{zz} component while the other two are only slightly modified, Table 1. The change in g_{zz} is in line with a simple physical picture: the polaronic distortion will effectively increase the electric field the radical is exposed to, very much as found when moving the radical from the terrace to low coordinated sites, such as edges. Note that the $O_2^{\cdot-}-Mg$ distances are much shorter on the thin film or on edge sites of powders than on the flat terraces of bulk MgO powder, Table 1. The resulting increased electric field in turn gives rise to an increase in the

energy difference between the two π orbitals of the oxygen radical. As the shift of g_{zz} component away from the free electron value is given by $g_{zz} = g_e + 2[\lambda^2/(\lambda^2 + \Delta^2)]^{1/2}$,[15] where λ is the spin orbit coupling constant and $\Delta = 2\pi_g^y - 2\pi_g^x$, the increase in Δ because of the increased electric field will lead to the expected decrease in the g_{zz} component. Consequently, the observed decrease of the g_{zz} component for the thin film results from the polaronic distortion.

In summary, the results presented herein are the first unambiguous demonstration for the spontaneous activation of molecular oxygen forming an $O_2^{\cdot-}$ radical upon adsorption on a stoichiometric, low-energy oxide surface, on a metal support, and confirm the theoretical predictions. The analysis of the g-tensor components of an MgO film on a Mo(001) surface and comparison with the results on MgO powders provide the first experimental evidence that stabilization of the oxygen radical cation is by means of polaronic distortions of the MgO lattice, which is only feasible for ultrathin films of a few monolayers thickness.

Methods Section

EPR experiments were performed on a MgO(001) film of various thickness grown on a Mo(001). The preparation follows methods described in literature.[16,17] In brief, the Mo substrate was cleaned by oxidation with O_2 at 1500 K and subsequent flashes to 2300 K. The MgO films were prepared by deposition of Mg in an oxygen atmosphere (1×10^{-6} mbar) at a substrate temperature of 600 K and a rate of 1 ML MgO/min. The films were subsequently annealed at 1200 K for 10 min. The EPR spectra were measured at 30 K with a microwave power of 2 mW in a TE_{102} cavity using a modulation amplitude of 4 G. Details of the experimental setup are described elsewhere.[18]

For the calculations of the g-tensor we used embedded cluster models and DFT calculations using the B3LYP hybrid functional.[19,20] The basis sets used are 6-31G on Mg, 6-31G* on the O atoms of MgO; for the O_2 molecule we used 6-311 + G* (geometry optimization) and EPR-II (EPR parameters). For the determination of the g-tensor we used the spin-orbit perturbation strategy in the scheme proposed by Neese,[21] and implemented in the code Gaussian03.[22] The structure of O_2 adsorbed on MgO/Mo(100) thin films was determined with plane wave periodic calculations using the VASP code[23,24] (PW91 exchange-correlation functional,[25] energy cut-off of 400 eV, projector augmented wave method[26]).

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