Autocatalytic partial reduction of FeO(111) and Fe₃O₄(111) films by atomic hydrogen

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Abstract

The interaction of atomic hydrogen with thin epitaxial FeO(111) and Fe₃O₄(111) films was studied by TDS, XPS and LEED. On the thin, one Fe-O bilayer thick FeO film, partial reduction occurs in two steps during exposure. It ends after removal of ¼ monolayer (ML) of oxygen with a 2×2 pattern appearing in LEED. This FeO_{0.75} film is passive against further reduction. The first reduction step saturates after removal of ~0.2 ML and shows autocatalytic kinetics with the oxygen vacancies formed during reduction causing acceleration. The second step is also autocatalytic and is related with reduction to the final composition and an improvement of the 2×2 order. A structure model explaining the two-step reduction is proposed. On the thick Fe₃O₄ film, irregular desorption bursts of H₂O and H₂ were observed during exposure. Their occurrence appears to depend on the film quality and thus on surface order. Because of the healing of reduction-induced oxygen vacancies by exchange of oxygen or iron with the bulk, a change of the surface composition was not visible. The existence of partially reduced oxide phases resistant even to atomic hydrogen is relevant to the mechanism of dehydrogenation reactions using iron oxides as catalysts.

Key words: Low energy electron diffraction, X-ray photoelectron spectroscopy, temperature programmed desorption, catalysis, surface chemical reaction, hydrogen atom, iron oxide

1. Introduction

Iron oxides, widespread in nature, are of interest to many scientific disciplines from geology to biology [1]. The reduction of iron oxides is inevitable in many processes, such as metallurgy, corrosion, and heterogeneous catalysis. It was long found that the very rapid dissolution of the passive iron oxides film on iron involves a reductive mechanism [2]. The surface reduction, together with coke formation, is responsible for the deactivation of the iron oxide-based catalyst for the dehydrogenation of ethylbenzene to styrene [3,4]. Because of their relevance for corrosion processes, the reduction of iron oxides in solution has been extensively studied and a clear understanding of the mechanism and kinetics is acquired [5]. However, fundamental understanding of iron oxide reduction by gas phase hydrogen is poor.

Most fundamental understanding of the gas-solid interactions comes from surface science studies of relevant model systems under ultra-high-vacuum (UHV) conditions. Very little is known about the interaction of hydrogen with well-characterized single-crystal iron oxides. The nearly stoichiometric, well ordered α -Fe₂O₃(0001) surface is inert towards molecular hydrogen at room temperature and interaction occurs only at defects [6]. Thus it is difficult to approach the reduction of iron oxides by employing molecular hydrogen. The reason is, of course, the high dissociation energy of H₂ (432 kJ/mol). Atomically adsorbed hydrogen, OH groups or protons are formed in catalytic dehydrogenation reactions or during electrochemical reduction. Therefore it makes sense to study the interaction of surfaces with atomic hydrogen H_{at} which should be able to interact with almost any surface. Since this interaction may be violent, defect formation and other structural changes may be expected. It has been shown that Ni(111) exposed to H_{at} under UHV condition can form bulk hydrogen species, which show a unique catalytic activity towards hydrogenation of hydrocarbons [7]. H atoms were also reported to readily adsorb on the ZnO(0001) surface [8,9].

Here we present a surface science study on the interaction of atomic hydrogen with iron oxides. We observe an autocatalytically accelerated partial reduction of the oxides. This represents a new type of autocatalytic surface reactions, different to autocatalytic reactions of or between adsorbates studied so far like decomposition of formic acid [10], [11] acetic acid [12] [13-15] or the reactions of CO with NO [16-21], NO with H₂ or NH₃ [17,22-24] and H₂ with O₂ [25].

After the experimental section, results on the interaction of H_{at} with a thin epitaxial FeO(111) film are presented and discussed. It will be shown that this model system is easy to analyse and allows to understand the finally presented phenomena on a thicker epitaxial Fe₃O₄(111) film more clearly.

2. Experimental

The experiments were performed in an ultrahigh vacuum (UHV) chamber with a base pressure in the 10^{-11} mbar range. It was equipped with a display LEED optics (Omicron), a hemispherical electron energy analyser (Phoibos 150, Specs), a dual anode X-ray source (VSW, used line Al $K\alpha$) for XPS and a quadrupole mass spectrometer (QMS, Balzers Prisma) for TPD. The QMS was equipped with an entrance cone (3mm diameter) so that only gas from the sample center could enter the QMS directly. Signals are uncalibrated and shown as measured.

A Pt(111) sample (9 mm diameter, 1.5 mm thick) with type K thermocouple spot welded to its edge was mounted on a sapphire support which could be introduced into the chamber via a transfer system [26]. The epitaxial oxide films were prepared as described earlier [26] by evaporating iron from an Fe wire wrapped around a heated W filament, followed by a proper oxidation cycle in 10^{-6} mbar O_2 . For the FeO(111) film, about 1 ML Fe was evaporated and oxidized at 1000 K which resulted in a film one Fe-O bilayer thick [27]. Its structure was checked by LEED and corresponded to the structure typical for the full bilayer (structure S2 according to [27]). The Fe_3O_4 (111) film was prepared by sequences of Fe depositions, 5-10 ML each, followed each time by short oxidation at about 900 K. Finally, the film was oxidized at slowly increasing T with $T_{max}=1000$ K until LEED showed a clear pattern. No signal from the Pt substrate could be detected in XPS. The film was thus at least about 10 nm thick.

A high efficiency source for atomic hydrogen (H_{at}) was constructed following the ideas of Bischler and Bertel [28]. The hydrogen gas passes through a W capillary the tip of which is heated by electron bombardment to about 2000 K resulting in a high degree of dissociation. The capillary is surrounded by a copper heat shield. At the sample position 4 cm in front of the capillary, the diameter of the H_{at} jet is large enough to yield a fairly homogeneous exposure. Given exposure values (in Langmuir units, 1 L = 1.33×10^{-6} mbar s) refer to the H_2 background pressure and are relative values concerning H_{at} . The actual exposures to H_{at} are unknown but from the observed reaction rates we can conclude that they have a similar magnitude. Thermal desorption spectra were taken at a heating rate of 4.3 K s^{-1} .

In the case of FeO, exposures were performed at 300 K. In order to separate the unavoidable desorption of H_2 from the heater (filament and its surrounding) from sample desorption, the sample was cooled to 230 K before starting TPD. The desorption peak from the heater extended up to about 330 K but since its shape was fairly independent of the preceding exposure to H_{at} , it could be subtracted from the TPD traces. H_2O did not desorb from the heater. Since both H_2 and H_2O are main constituents of the residual gas, a linear background was subtracted. Especially the H_2O background depended on the chamber history and varied within a factor of 5. This is the reason for different noise levels.

In the case of Fe_3O_4 , exposures were performed at 355 K and TPD started after cooling to 300 K.

3. Results and discussion

3.1 H_2 on FeO(111) and Fe_3O_4 (111)

The interaction of molecular hydrogen with the oxide films was tested by exposing them at room temperature to 1000 L H_2 . The changes of the LEED patterns and of the XP-spectra of O 1s and Fe 2p are negligible and we ascribe them rather to the residual water formed by reaction with the chamber walls during exposure than to the direct interaction with H_2 . One reproducible effect was an apparent shift of all XP-spectra by about 0.1-0.2 eV towards higher binding energy directly after pumping off the admitted gas. This shift disappears within about 30 min without any other spectral changes. Therefore we assign it to reversible H_2 -induced work function changes in the analyser. Similar shifts were also observed after exposure to H_{at} which generates a high H_2 background pressure.

3.2 H_{at} on FeO(111) - results

Figure 1 shows background-corrected TPD results for desorption of H_2 and H_2O from the FeO(111) film exposed at room temperature to increasing amounts of H_{at} between 0.2 and 10 L. After each exposure and TPD run, the film was reoxidized and it was checked by LEED that the clean film pattern was reestablished. While the desorption of H_2 (fig. 1 A) follows a quite irregular pattern, the desorption of H_2O (fig. 1 B) shows one peak which shifts from ~ 430 K at 0.2 L to ~ 380 K at 0.75 L which may be ascribed to a 2nd order recombinative desorption reaction.

Surprisingly, desorption of both H_2 and H_2O drops to very low values at 1 L and increases again for higher exposures. H_2O desorption ceases completely for exposures beyond about 3 L. H_2 desorption does not cease but obviously its mechanism changes. The irregular desorption behavior finishes at about 4 L and instead a clear and sharp peak develops at 330 K (4 L) which eventually shifts to 350 K (50 L). This behavior is very different to that of H_2 desorption from Pt(111) [29] where a H_2 desorption peak appears initially at 382 K and shifts with increasing exposure to lower T (e.g. 318 K after 10 L). We can therefore conclude that (within the sensitivity of TPD) no open Pt(111) areas have formed. Although with a changed composition (see below), the FeO_x film is still closed, even after high exposures. As will be shown, the behavior up to ~ 3 L is related with changes in film composition and structure while the regular behavior beyond ~ 5 L is related with a stable film without further changes.

The areas of the TPD traces of fig. 1 A,B were integrated and are displayed in fig. 2. While fig. 1 represents a selection of measured traces, fig. 2 comprises all measured data including repeated measurements for certain exposures. The scatter in the H_2O data is relatively weak. The stronger scatter in the H_2 data is mainly due to the larger uncertainty in background subtraction caused by the broad and irregular shape of the desorption traces below about 5 L. While H_2O desorption is strong and H_2 desorption is weak below 1 L, the intensity ratio is inverted in the second cycle between 1 L and 3 L. The change in

the desorption mechanism of H_2 (broad and irregular desorption traces, strong scatter in the intensities below and well defined and sharp traces beyond about 5 L) is also reflected in fig. 2 C. It should be stressed, however, that figs. 1 and 2 do not give actual relative intensities of H_2 and H_2O since their relative sensitivities for QMS detection are not known.

Figure 1: TPD traces for desorption of H_2 (A) and H_2O (B) after exposure of a thin FeO film to atomic H_{at} to the indicated amounts (in Langmuir units).

Figure 2: Integrated intensities from all measured TDP traces. (A), (B): Low exposure range for H_2O and H_2 . (C): Complete exposure range for H_2 .

While TPD gives only information about the species leaving the surface upon heating, XPS gives information on the species existing on the surface before and after heating. Fig. 3 A shows representative O 1s spectra after different exposures and also after a flash to 800 K, corresponding to the situation after TPD. Also here, the film was reoxidized and checked by LEED after each cycle of exposure and flash. The background increases towards lower BE because of the tail of the Pt $4p_{3/2}$ substrate peak (BE=520 eV) which is strongly visible because the FeO film is only one Fe-O bilayer thick. This is also the

reason why the O 1s peak is weak and the noise relatively high. The O 1s peak shape on the clean film (fig. 3 B, curve a) is more asymmetric than in thick oxide films. This may in part be due to the interaction with the metallic Pt substrate (see e.g. [30]) and in part to the site inhomogeneity induced by the misfit between the FeO film and the Pt substrate [27].

Figure 3: O 1s spectra after exposing the thin FeO film to atomic H_{at} and after subsequent flashing to 800 K. (A) Different exposures. (B) Analysis of XP spectra. (a) clean with background line; (b) after exposure to 0.75 L (open circles), after background subtraction (full circles) and decomposition into two components; also shown is the residual of curve fitting; (c) after flash. (C) Exposure dependence of the total O 1s intensity and the intensity of the OH component. The dotted line is an estimation of the contribution from restructuring (see text).

After exposure (fig. 3 A), the O 1s emission consists of a main peak at 529.5 eV which is typical for the oxide film and a shoulder at 531.3 eV which we ascribe to OH groups. The comparison with the spectra after flash where the OH contribution has disappeared, shows immediately that the OH contribution is strong at 0.5 L and smaller at 1 L. Beyond 1 L, the situation is more complex as the detailed analysis will show. Further, it is evident that the overall peak area decreases with exposure indicating oxygen loss already during exposure.

In order to quantify these observations, the emission was analysed as demonstrated in fig. 3 B for an exposure of 0.75 L. Curve (a) shows the clean surface spectrum and the background line. Curve (b) is after exposure (open circles) and after background subtraction (full circles). The latter curve is decomposed into two contributions using the averaged background-corrected clean surface spectrum for the component shape. The energy difference between main component (FeO) and shifted component (OH) turned out to be 1.75 ± 0.1 eV. It was then fixed to 1.75 eV for the fit of peaks at all exposures. Although all hydrogen should be removed by flashing, the shape of the O 1s emission after flash is different to that of the initial clean surface. It is broader and tails out towards higher BE. In the standard peak decomposition procedure (two components, $\Delta E = 1.75$ eV), this gives rise to an apparent OH component but the fit is not satisfying which suggests that this component has another reason. We ascribe this change of the peak shape to restructuring as will be discussed in detail below. Since oxygen is already lost during exposure, restructuring-induced components may form after exposure and will disturb the real OH intensity. Because of the limited resolution of standard XPS and the scatter in the data of fig. 3 A, we did not try to consider a restructuring-induced component in peak fitting.

Fig. 3 C summarizes the results of O 1s peak analysis. The upper curves give exposure dependence of the integrated total O 1s intensity after exposure (open circles) and after the following flash (crosses). Up to about 0.5 L, the intensity after exposure is almost constant, drops then steeply to $\sim 80\%$ which is reached at 1 L, forms a shoulder and reaches a final value of $\sim 75\%$ at 2-3 L. Since the film initially consisted of 1 ML of oxygen, this reduction means that $\frac{1}{4}$ ML of oxygen has left. After flash, the intensity drops linearly and reaches the same final value at 1-1.2 L. The difference between both curves represents the oxygen leaving during flash and in fact it would have two maxima, separated by a minimum at 1 L, very similar to the TPD intensity of H_2O (fig. 2 A).

The lower curve in fig. 3 C represents the intensity of the OH component from peak fitting. Initially it increases steeply, passes through a minimum at 1 L and increases again at higher exposures. It is likely that the interfering component from restructuring increases along with oxygen removal. Tentatively, the dotted line may account for its contribution. As reliable result we conclude that the OH component initially forms a maximum and decreases at 1 L where also TPD showed a minimum of the adsorbate coverage.

Figure 4: (A) Some Fe 2p_{3/2} spectra after exposing the thin FeO film to the indicated amounts (in L) of atomic H_{at}. The marks c, e, f indicate peak maxima for the clean (squares, left curve), exposed (line, right curve) and flashed (triangles, center curve) surface. The marks J, W indicate peak positions for FeO and metallic Fe from literature: J=Joseph et al. [31], W= Weissenrieder et al. [32]. (B): Exposure dependence of the position of the low BE slopes (half maximum) from (A).

Corresponding Fe 2p_{3/2} data are presented in fig. 4. The peak intensities are essentially unaffected by exposure which proves that no iron is removed by interaction with H_{at}. However, the peak positions change. For the 5 L spectra, the positions of the maximum of the clean surface, after exposure and after flashing are marked. Even more clearly, the shift can be seen at the position of the low-BE edge of the spectra. Peak positions for the thin FeO film and for metallic iron from literature are indicated by the bars on top. Even for high exposures, the position does never reach that of metallic iron. The exposure

dependence of the edge shift is plotted in fig. 4 B. Below about 1 L, the shifts after exposure and after flash are similar. Beyond 1 L, however, the shift after exposure increases further and saturates at 1.5-2 L while the shift after flash remains constant. The different exposures for peak shift saturation after exposure and after flash agree fairly well with the different exposures where the O 1s intensity decrease saturates (~ 1.2 L and ~ 2 L, fig. 3 C).

Fig. 5 shows representative LEED patterns for the clean FeO film, after exposure to 2 L H_{at} and after flash. The floreted satellite pattern of the clean surface is a result of multiple scattering of Pt(111) and the FeO(111) adlayer [27]. The solid rhomb represents the periodicity of the Pt(111) substrate, the dashed rhomb that of the FeO(111) film. After exposure, the satellite pattern has disappeared completely. The intense spots are at the Pt(111) positions. New diffuse spots have appeared which correspond to a 2×2 -pattern. As demonstrated by the dotted lines, its periodicity does neither coincide with the Pt(111) lattice nor with that of the original FeO film. We assign it to the partially reduced $FeO_{0.75}$ film. Compared to the original FeO film, the real space unit cell of $FeO_{0.75}$ is thus slightly smaller than twice the FeO unit cell which means that the film is slightly contracted. From the width of the 2×2 spots, we can conclude that the $FeO_{0.75}$ domains are only about 3-4 nm wide. At the exposure of 2-3 L, these spots appear most clearly. At 1 L, they are elongated further along the main crystallographic directions suggesting domain sizes of only ~ 2 nm. The 2×2 periodicity is stabilized by adsorbed hydrogen and disappears after flashing. Intense FeO spots reappear but they are not sharp and the floreted satellite pattern does not reappear which indicates a reduced long-range order. Reoxidation at 1000K without deposition of iron leads to reestablishment of the floreted clean FeO pattern which also proves that no iron was removed by exposure to H_{at} .

Figure 5: LEED pattern ($E_p=60$ eV) of FeO, clean, after exposure to 2 L H_{at} and after flash (800 K). The unit cells are indicated. Solid line: Pt(111) periodicity; dashed: Periodicity of the thin FeO(111) film; dotted: 2×2 periodicity of reduced $FeO_{0.75}$ film corresponding to the diffuse superstructure spots.

3.3 H_{at} on FeO(111) - discussion

While the Fe 2p intensity (fig. 4 A) is not affected by exposure to H_{at} or by annealing, the O 1s intensity decreases already during exposure (fig. 3 C) so that a partially reduced FeO_x film ($1 > x > 0.75$) is formed. This oxygen removal process shows unusual behavior. According to the decrease of the O 1s intensity with exposure, the initial removal rate is low, accelerates around 0.5 L, stops at 1 L and proceeds to the final composition $FeO_{0.75}$ at 2-3 L. Between 0 and 1 L, this behavior is characteristic for an autocatalytic process with saturation after 1L. The kinetics is similar to that of oxide reduction in electrochemical pitting corrosion of stainless steel which recently was identified as due to an autocatalytically accelerated growth in the number of active pits [33].

The autocatalytic acceleration of this reduction explains also the unusual results of TPD (fig. 1) and of the OH intensity (fig. 3 C). Initially, the OH intensity on the surface increases as does the intensity of H_2O desorbing in TPD. At 0.5 L, however, the reduction during exposure gets so violent that more and more OH groups are consumed and at 1 L almost no adsorbates are left for desorption in TPD.

Beyond 1 L, a second reduction cycle starts. It also shows the characteristics of an autocatalytic process but from the different H_2/H_2O ratio in the desorption intensities (fig. 2) we conclude that its mechanism is different. Although the removed amount of oxygen is much smaller than in the first period, it needs a higher exposure (1-2 L) for saturation.

During the reduction, the film restructures. A 2×2 pattern appears in LEED which starts to be visible at 1 L in form of streaky features and is developed best at 2-3 L. This restructuring during exposure which probably continues during annealing may affect the desorption of H_2 which competes with reduction by H_2O desorption. This explains the irregular shape of the TPD traces for H_2 in fig. 1 A. Despite reduction and restructuring, the FeO_x film remains closed.

Starting from the observations that the autocatalytic reduction results in a closed oxide film with 2×2 periodicity and poor long-range order which is accompanied by a drop of the oxygen coverage from 1 ML to 0.75 ML (corresponding to a film composition of $FeO_{0.75}$), we propose the following model.

Starting points for the reduction are oxygen vacancies. These may either exist as structural defects from the beginning or they are formed at a comparatively slow rate during exposure to H_{at} , leading to water desorption at a low rate. Since the FeO films initially have a high degree of order [27,34], the mechanism with slow defect production during exposure is more likely.

The missing bonds at a vacancy induce a stabilization of the Fe-O bonds surrounding it (grey O-atoms in fig. 6 A) but the formation of a 2×2 periodicity suggests that the next-nearest O-atoms in direction of the O-rows are destabilized (dotted O-atoms in fig. 6 A) and can be removed more easily by reaction with two adsorbed H atoms (process (1) in fig. 6 A). This results in a neighboring second vacancy. It results further in an increase of the concentration of destabilized O-sites (fig. 6 B) which in turn increases the reaction rate. This explains the autocatalytic acceleration of the reduction. Process (1) in fig. 6 A assumes that the destabilized O adsorbs one H atom, forming an OH group and reacts with another H atom adsorbed on a neighboring O. An alternative would be that H also adsorbs relatively weakly at the O vacancy and can react with a destabilized OH (process (2), fig. 6 B). The concentration of such H atoms would increase with the concentration of vacancies and could result in an autocatalytic acceleration as well.

Figure 6: FeO(111) thin film, mechanism of autocatalytic reduction and restructuring. For explanation see text.

We suggest that the removal of destabilized O atoms in form of H_2O occurs at RT while OH groups formed on the undisturbed FeO surface are more strongly bound. At RT their desorption as H_2O is quite slow but may account for initial vacancy formation. The main portion desorbs during TPD as H_2O , starting initially at 350K (0.2L) with the onset shifting to $\sim 320K$ at 0.5L (Fig. 1 B). Below 1L, the competing recombinative desorption of H_2 is relatively weak (Fig. 2 B).

Eventually, the described process would result in the autocatalytically accelerated formation of 2×2 domains growing around the original vacancies. This comes to a first stop when neighboring domains meet and no more destabilized O atoms exist. If the meeting domains are in phase, they coalesce, otherwise, antiphase domains form which are separated by boundaries consisting of oxygen double rows (B_1 , B_2 in fig. 6 C). This is the situation after exposure to 1L. In LEED, 2×2 spots have not yet formed but streaks are visible indicating domains only about $\sim 2nm$ wide. We conclude from this that the density of original vacancies as domain nuclei is relatively high, surely higher than the vacancy density of the original film. This supports the idea of initial slow vacancy formation under the influence of H_{at} exposure.

This explains also why the floreted satellite pattern of the clean film is already destroyed after exposure to only 1L. The satellite pattern is a result of a long-range coincidence structure of the FeO film with the Pt substrate. The atomic rows of the FeO film are slightly rotated with respect to the substrate rows and coincidence sites are reached after about 8 FeO units and 9 Pt units, respectively (see [27,34] for details). The 2×2 domains formed after reaction with H are much smaller and destroy the original long-range order.

Because of the antiphase domain boundaries, the ideal oxygen coverage of 0.75 ML is not reached after exposure to 1L. Experimentally, fig. 3 C shows a plateau at ~ 0.8 ML. Further exposure causes a second slower reduction process. The final coverage of 0.75 ML is reached at 2-3 L where also the 2×2 pattern (fig. 5) is developed best. This process must be related to a movement of antiphase boundaries as represented schematically in fig. 6 C. If the marked O atoms of the two boundaries move in direction of the arrows into the positions marked 'A', the structure in fig. 6 D is formed with (in this example) three destabilized O atoms which then can readily be removed in the reduction process.

During oxygen removal, the bonding configuration of all O atoms remaining on the surface is eventually modified to the stabilized form. This restructuring may result in a changed O1s peak position and/or shape. Peak fitting under the assumption of two components at a fixed distance as we performed it (fig. 3) necessarily results in a contribution at the position of the OH component. This is the origin of the component apparently induced by restructuring (fig. 3 C, dotted curve).

The reciprocal space unit cell size of the 2×2 pattern in LEED seems to be slightly larger than half the original FeO periodicity suggesting a real space distance of the Fe atoms slightly smaller than in the undisturbed film. This contraction is compatible with the assumed stabilization of the O atoms and their reduced concentration which may allow a slightly denser packing. In this case, however, the film could be expected to tear up and expose some of the Pt substrate. Since there is no indication for this, we have to assume that the 2×2 domains remain small and are limited by disturbed domain boundaries which is in agreement with the 2×2 spot width indicating domains only 3-4 nm wide.

After an exposure to about 3L, the surface is passivated and no more water is formed. Only H_2 desorbs in TPD, forming the sharp peak observed in fig. 1 A at high exposures. This tells us that the $FeO_{0.75}\text{-}2\times 2$ structure is quite stable even in the presence of atomic H_{at} radicals. Concerning the mechanism of catalytic dehydrogenation of ethylbenzene to styrene over iron oxides this is a remarkable result. In model catalysis experiments over Fe_2O_3 [4,35] it was found that the H formed on the surface reduces the catalyst to Fe_3O_4 . However, the produced amount of styrene and thus also of hydrogen was by about two orders of magnitude higher than explainable by a stoichiometric reduction reaction with oxygen from the catalyst. It was concluded that also the desorption of hydrogen as H_2 must have occurred which, however, could not be analysed directly in that study. In the present investigation we clearly see that surface phases may exist which are stabilized against reduction by H_{at} and may desorb molecular H_2 .

Although flashing does not change the composition concerning Fe and O, the 2×2 spots disappear and the original FeO periodicity gets strong again. This supports that the adsorbed hydrogen before flashing stabilizes the domain boundaries of the contracted 2×2 structure.

Figure 7: LEED pattern ($E_p=60$ eV) of the $Fe_3O_4(111)$ film, clean (A), unit cell marked, and after exposure to 10 L atomic H_{at} (B). Dotted circles in (A) mark minority contribution from $Fe_2O_3(0001)$. (C) Surface termination by $1/4$ ML of iron (dark circles) on a full oxygen layer (large bright circles). O_b atoms are coordinated to surface iron, O_a atoms are not.

Figure 8: Typical development of the H_2 and H_2O signal in QMS during exposure of Fe_3O_4 at 355 K to a constant H_{at} pressure of 1.3×10^{-8} mbar.

Figure 9: (A) TPD traces for H_2O desorption from $\text{Fe}_3\text{O}_4(111)$ after the indicated exposures to atomic H_{at} at 355 K. Dashed line: Approximate background for the 5 L curve. (B) Exposure dependence of the total TPD intensity from (A), background corrected. The error bar is an estimation considering the uncertainty of background subtraction.

Figure 10: O 1s and Fe 2p signals after exposure of $\text{Fe}_3\text{O}_4(111)$ to 4.4 L H_{at} . (A) Decomposition of the O 1s emission into components of the shape on the clean surface. (B) The maxima at about -708.5 and -723 eV in the difference curve indicate a small reduction-induced component after exposure.

We may now understand the dependence of the Fe 2p peak shift on exposure and flashing (fig. 4). It may result from the combined action of oxygen removal and hydrogen adsorption which both contribute to Fe reduction. Below 1 L, the Fe 2p shift is mainly caused by the oxygen removal. Flashing has a minor effect because not much hydrogen was adsorbed (in agreement with TDS). Beyond 1 L, further oxygen removal is slow and more hydrogen remains adsorbed. Its removal by flashing causes the observed reduction of the peak shift.

3.4 H_{at} on $\text{Fe}_3\text{O}_4(111)$ - results

Fig. 7 A shows the LEED pattern of the fresh $\text{Fe}_3\text{O}_4(111)$ film. Apart from the intense and sharp $\text{Fe}_3\text{O}_4(111)$ pattern, weak and diffuse spots appear on this film which correspond to a minority contribution from some $\text{Fe}_2\text{O}_3(0001)$ domains. This may happen during preparation since Fe_2O_3 is the thermodynamically stable phase under the applied preparation conditions [36] while Fe_3O_4 is metastable and forms since oxidation to Fe_2O_3 is kinetically hindered. We do not consider the Fe_2O_3 contribution further. After exposure to atomic H_{at} (fig. 7 B), the only change is a small general reduction of spot intensities.

Fig. 8 shows a characteristic time dependence of H_2 and H_2O evolution during exposure to 1.3×10^{-8} mbar H_{at} (H_2 background pressure measured). At room temperature, H_2O is not yet completely desorbed from $\text{Fe}_3\text{O}_4(111)$ [37] and might block the surface reaction. Therefore a temperature of 355 K was chosen during exposure. At the marked position, the heating of the W-capillary and thus H_{at} production was switched on. The pressure drop is related to reaction of a part of the formed H_{at} with the sample and the chamber walls. After about 500 s, the H_2 evolution suddenly increases and drops back abruptly to the background intensity. We ascribe this to H_2 desorption from the sample. Further H_2 bursts occur irregularly concerning time

and intensity. The H₂O evolution shows a corresponding behavior. On a constantly increasing residual gas background originating from reaction of hydrogen with oxides on the chamber walls, desorption bursts appear with a 1:1 correspondence to the H₂ bursts.

On freshly prepared Fe₃O₄ films, the first desorption burst did not always appear at the same exposure. We even had films where no burst had appeared within 1000 s.

In a separate set of experiments, XPS data were taken before and after exposure at 355 K, then a TPD run was performed, followed by taking final XPS data. Fig. 9 A shows TPD data for H₂O desorption after exposure in the range from 4 to 6.4 L H_{at}. Generally, a broad desorption feature with two maxima at about 440 and 560 K appears superimposed on a background of varying slope. For 5 L, this background happens to start from a very high intensity and drops during the measurement. The H₂O desorption peak superimposed on it is very small. We ascribe the high and decreasing background to the water desorbed in a burst as observed in fig. 8 immediately preceding the TPD measurement. This burst removes a part of the H₂O from the surface which explains why so little desorbs in the following TPD run. Fig. 9 B shows the exposure dependence of the integrated TPD intensities of H₂O. The intensity increases initially, drops around 5 L, recovers and shows a second less intense drop at 6 L. Because of the high background after 5 L in fig. 9 A, the corresponding point at 5 L in fig. 9 B has a large uncertainty.

As an example, fig. 10 shows O 1s and Fe 2p spectra and their analysis before and after exposure to 4.4 L H_{at}. The emission is dominated by the bulk contributions and is only very weakly influenced by adsorption. The Fe 2p emission (fig. 10 B) shows only a weak reduction-induced contribution. The O 1s emission (fig. 10 A) can be fitted excellently by two components with the shape of the clean surface emission, separated by 1.8-1.6 eV which we again ascribe to the bulk and the OH component. The exposure dependence of the OH peak shift and the relative OH intensity is displayed in fig. 11. The OH intensity increases with exposure and there is no prominent feature at 5 L which would correspond to the minimum in the TPD intensity in fig. 9 B. If anything, there is a small step at 5 L. Probably, not all water was desorbed in the desorption burst during exposure.

We can perform a quantitative estimation of OH coverage using electron mean free paths from literature. The ratio of the OH- to total intensity is given by

$$J_{OH} / J_{tot} = (1 - e^{-d/\lambda}) / e^{-d/\lambda},$$

with λ the electron mean free path and d the thickness of the OH layer. For electron kinetic energies beyond ~100 eV, the energy dependence of λ can be approximated by

$$\lambda \approx 0.054 \sqrt{E}; \quad (\lambda \text{ in nm, } E \text{ in eV [38]}).$$

The final relative OH-intensity in fig. 11 is ~4.3% of the total intensity which corresponds to a thickness of ~0.05 nm. The distance between two O-layers in Fe₃O₄ is 0.246 nm. The OH intensity corresponds thus roughly to 1/5 of an oxygen layer. If it were 1/4, which is well within the error limit of this estimation, its concentration would correspond to one OH per surface unit cell. This fits excellently with what we know about dissociative water adsorption on Fe₃O₄ [37,39,40]: Hydrogen is most tightly bound to the so-called O_a sites (see fig. 7 C) while the OH in case of water dissociation binds to Fe. The concentration of O_a sites is 1/4 ML.

This is surprisingly also the same concentration as the vacancy concentration in the (2x2) structure on FeO.

Figure 11: Exposure dependence of the shift of the OH component on Fe₃O₄ with respect to the bulk component and of its relative intensity in % of the total O 1s intensity.

3.5 H_{at} on Fe₃O₄(111) - discussion

We suggest the following model for Fe₃O₄:

H_{at} forms OH groups on the iron oxide films. On the thin FeO layer, they react (autocatalytically accelerated) to H₂O which desorbs and eventually results in the 2x2 vacancy structure. On Fe₃O₄, a similar mechanism may work but the desorption in form of H₂O is more difficult, probably because of two reasons: First, the initial defect formation from which the autocatalytic reduction starts may be more difficult. Second, H adsorbs preferentially on O_a sites (see fig. 7 C) which are second-nearest neighbors. In order to form H₂O, a second H atom must be adsorbed on a neighboring O_b site. Since adsorption on O_b sites is weaker, this does not happen frequently. Therefore, H₂O desorption happens only incidentally on the well-ordered initial surface which is the reason why the first desorption burst in fig. 8 comes so late. We even had Fe₃O₄

films where no burst occurred within the measuring time. The appearance of desorption bursts suggests that desorption of one H₂O and thus removal of one lattice oxygen atom destabilizes neighboring OH groups by strain effects and accelerates desorption autocatalytically. The first desorption burst induces some disorder which makes further desorption bursts easier. The desorption bursts have a variable integral intensity which suggests that usually not the whole surface contributes to them. H₂O desorption leaves O-vacancies at the surface which at 355 K may relatively quickly be removed by diffusion of oxygen from the bulk or by diffusion of surface iron into the bulk, followed by surface rearrangement. Apart from some disorder which decreases the intensity of the sharp LEED spots only slightly, the surface composition remains therefore almost constant.

4. Conclusions

The observed partial reduction of a thin FeO film grown on a Pt(111) substrate by exposure to gaseous atomic hydrogen H_{at} represents a type of autocatalytic surface reactions which so far has only been observed in electrochemical pitting corrosion of oxide films [33]. A mechanism is proposed according to which reduction starts at oxygen vacancies. Since reduction creates further vacancies, reduction accelerates autocatalytically. An exciting detail observed here is that the reduction stops by forming an ordered layer with 2×2 periodicity in LEED and an oxide composition of FeO_{0.75} which is passive even against atomic H_{at}. Further reduction to metallic iron does not occur or is at least several orders of magnitude slower. Hydrogen is still adsorbed but desorbed as H₂ and not as H₂O. An advantage was that this oxide film was only one Fe-O bilayer thick so that there were no bulk contributions in the XP spectra which would make their analysis difficult. Further, the surface composition was not influenced by diffusion from or to deeper layers.

Insofar, the study of the thin FeO film can be considered a model case for the study of the thick Fe₃O₄ film. Irregular bursts of H₂ and H₂O desorption were observed during exposure of this film to H_{at}. Especially the onset of the first desorption burst appears to depend on the quality of the starting film which suggests that defects are necessary and that defect formation by interaction with H_{at} is more difficult than on the thin FeO film. Neither the overall surface composition nor the overall order is strongly affected by desorption bursts. From this we conclude that surface vacancies are quickly annihilated by exchange of oxygen or iron with the bulk, at least as long as the overall reduction is not too strong.

The observation of oxide passivation against reduction is of interest for the mechanism of dehydrogenation reactions over oxide catalysts like the dehydrogenation of ethylbenzene to styrene over iron oxide based catalysts [26]. After dehydrogenation, hydrogen remains on the surface which has to be removed in order to close the catalytic cycle. There is an ongoing debate if this can only occur by desorption of H₂O thus leaving behind an oxygen vacancy which has to be reoxidized in a further step (Mars-Van Krevelen mechanism) or if hydrogen can also desorb as H₂. Our study suggests that at least on iron oxides, surface phases may exist from which H₂ desorption is possible.

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