Autocatalytic partial reduction of FeO(1 1 1) and Fe_3O_4(1 1 1) films by atomic hydrogen

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Abstract

The interaction of atomic hydrogen with thin epitaxial FeO(1 1 1) and Fe_3O_4(1 1 1) 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 1/4 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 $\sim$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 Fe_3O_4 film, irregular desorption bursts of H_2O and H_2 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.
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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 oxide films 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 corro-

sion 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-Fe_2O_3(0 0 0 1) 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 H_2 (432 kJ/mol). Atomically adsorbed hydrogen, OH groups or protons are formed in catalytic

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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 [12–15]or the reactions of CO with NO [16–21], NO with H_2 or NH_2 [17,22–24] and H_2 with O_2 [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 Fe_3O_4(111) film more clearly.

2. Experimental

The experiments were performed in an ultra-high-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 AlKα) for XPS and a quadrupole mass spectrometer (QMS, Balzers Prisma) for TPD. The QMS was equipped with an entrance cone (3 mm 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

Fig. 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