



Iron oxide surfaces

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Abstract

The current status of knowledge regarding the surfaces of the iron oxides, magnetite (Fe_3O_4), maghemite ($\gamma\text{-Fe}_2\text{O}_3$), haematite ($\alpha\text{-Fe}_2\text{O}_3$), and wüstite (Fe_{1-x}O) is reviewed. The paper starts with a summary of applications where iron oxide surfaces play a major role, including corrosion, catalysis, spintronics, magnetic nanoparticles (MNPs), biomedicine, photoelectrochemical water splitting and groundwater remediation. The bulk structure and properties are then briefly presented; each compound is based on a close-packed anion lattice, with a different distribution and oxidation state of the Fe cations in interstitial sites. The bulk defect chemistry is dominated by cation vacancies and interstitials (not oxygen vacancies) and this provides the context to understand iron oxide surfaces, which represent the front line in reduction and oxidation processes. Fe diffuses in and out from the bulk in response to the O_2 chemical potential, forming sometimes complex intermediate phases at the surface. For example, $\alpha\text{-Fe}_2\text{O}_3$ adopts Fe_3O_4 -like surfaces in reducing conditions, and Fe_3O_4 adopts Fe_{1-x}O -like structures in further reducing conditions still. It is argued that known bulk defect structures are an excellent starting point in building models for iron oxide surfaces.

The atomic-scale structure of the low-index surfaces of iron oxides is the major focus of this review. Fe_3O_4 is the most studied iron oxide in surface science, primarily because its stability range corresponds nicely to the ultra-high vacuum environment. It is also an electrical conductor, which makes it straightforward to study with the most commonly used surface science methods such as photoemission spectroscopies (XPS, UPS) and scanning tunneling microscopy (STM). The impact of the surfaces on the measurement of bulk properties such as magnetism, the Verwey transition and the (predicted) half-metallicity is discussed.

The best understood iron oxide surface at present is probably $\text{Fe}_3\text{O}_4(100)$; the structure is known with a high degree of precision and the major defects and properties are well characterised. A major factor in this is that a termination at the $\text{Fe}_{\text{oct}}\text{-O}$ plane can be reproducibly prepared by a variety of methods, as long as the surface is annealed in 10^{-7} – 10^{-5} mbar O_2 in the final stage of preparation. Such straightforward preparation of a monophase termination is generally not the case for iron oxide surfaces. All available evidence suggests the oft-studied ($\sqrt{2} \times \sqrt{2}$) $\text{R}45^\circ$ reconstruction results from a rearrangement of the cation lattice in the outermost unit cell in which two octahedral cations are replaced by one tetrahedral interstitial, a motif conceptually similar to well-known Koch–Cohen defects in Fe_{1-x}O . The cation deficiency results in $\text{Fe}_{11}\text{O}_{16}$ stoichiometry, which is in line with the chemical potential in ultra-high vacuum (UHV), which is close to the

Abbreviations: AES, auger electron spectroscopy; AFM, atomic force microscopy; APDBs, antiphase domain boundaries; CEMS, conversion electron Mössbauer spectroscopy; CTR, crystal truncation rod; DBT, distorted bulk truncation; DFT, density functional theory; DFT+U, density functional theory with additional Hubbard U ; DOS, density of states; ESRF, European synchrotron radiation facility; FCC, face centred cubic; Fe_{oct} , octahedrally coordinated Fe cation; Fe_{tet} , tetrahedrally coordinated Fe cation; FWHM, full width at half maximum; GGA, generalized gradient approximation; GW, Greens function (G) with screened Coulomb interaction (W); HCP, hexagonal close packed; HREELS, high-resolution electron energy loss spectroscopy; HSE, Heyd–Scuseria–Ernzerhof; IPES, inverse photoemission spectroscopy; IRAS, infrared reflection absorption spectroscopy; L, Langmuir ($1\text{L} = 1.33 \times 10^{-6}$ mbar s); LEED, low energy electron diffraction; LEED IV, quantitative low energy electron diffraction; LEEM, low energy electron microscopy; LEIS, low energy ion scattering; MEIS, medium energy ion scattering; MBE, molecular beam epitaxy; MDS, metastable deexcitation spectroscopy; ML, monolayer; MRI, magnetic resonance imaging; nc-AFM, non-contact atomic force microscopy; NEXAFS, near edge X-ray absorption fine structure; OH, hydroxyl group; PBE, Perdew–Burke–Ernzerhof functional; $\text{PBE} + U$, Perdew–Burke–Ernzerhof functional with additional Hubbard U ; PDOS, partial density of states; PEEM, photoemission electron microscopy; PEC, photo-electrochemical; PES, photoemission spectroscopy; PLD, pulsed laser deposition; RF, radio frequency; RHE, reference hydrogen electrode; RHEED, reflection high energy electron diffraction; RMS, root mean square; SCV, subsurface cation vacancy; SMSI, strong metal support interaction; SP-LEEM, spin polarized low energy electron microscopy; STM, scanning tunnelling microscopy; STS, scanning tunnelling spectroscopy; SXRD, surface X-ray diffraction; TEM, transmission electron microscopy; TPD, temperature programmed desorption; TPR, temperature programmed reduction; TSMR, transition metal surface resonance; T_C , Curie temperature; T_V , Verwey transition temperature ($T_V = 125$ K); UHV, ultra-high vacuum; UPS, ultraviolet photoemission spectroscopy; V_O , oxygen vacancy; WGS, water–gas shift; XAS, X-ray absorption spectroscopy; XES, X-ray emission spectroscopy; XMCD, X-ray magnetic circular dichroism; XPS, X-ray photoelectron spectroscopy; XRD, X-ray diffraction; XSW, X-ray standing waves

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border between the Fe_3O_4 and Fe_2O_3 phases. The $\text{Fe}_3\text{O}_4(111)$ surface is also much studied, but two different surface terminations exist close in energy and can coexist, which makes sample preparation and data interpretation somewhat tricky. Both the $\text{Fe}_3\text{O}_4(100)$ and $\text{Fe}_3\text{O}_4(111)$ surfaces exhibit Fe-rich terminations as the sample seldedge becomes reduced. The $\text{Fe}_3\text{O}_4(110)$ surface forms a one-dimensional (1×3) reconstruction linked to nanofaceting, which exposes the more stable $\text{Fe}_3\text{O}_4(111)$ surface. $\alpha\text{-Fe}_2\text{O}_3(0001)$ is the most studied haematite surface, but difficulties preparing stoichiometric surfaces under UHV conditions have hampered a definitive determination of the structure. There is evidence for at least three terminations: a bulk-like termination at the oxygen plane, a termination with half of the cation layer, and a termination with ferryl groups. When the surface is reduced the so-called “bi-phase” structure is formed, which eventually transforms to a $\text{Fe}_3\text{O}_4(111)$ -like termination. The structure of the bi-phase surface is controversial; a largely accepted model of coexisting Fe_{1-x}O and $\alpha\text{-Fe}_2\text{O}_3(0001)$ islands was recently challenged and a new structure based on a thin film of $\text{Fe}_3\text{O}_4(111)$ on $\alpha\text{-Fe}_2\text{O}_3(0001)$ was proposed. The merits of the competing models are discussed. The $\alpha\text{-Fe}_2\text{O}_3(1\bar{1}02)$ “R-cut” surface is recommended as an excellent prospect for future study given its apparent ease of preparation and its prevalence in nanomaterial.

In the latter sections the literature regarding adsorption on iron oxides is reviewed. First, the adsorption of molecules (H_2 , H_2O , CO , CO_2 , O_2 , HCOOH , CH_3OH , CCl_4 , CH_3I , C_6H_6 , SO_2 , H_2S , ethylbenzene, styrene, and Alq_3) is discussed, and an attempt is made to relate this information to the reactions in which iron oxides are utilized as a catalyst (water–gas shift, Fischer–Tropsch, dehydrogenation of ethylbenzene to styrene) or catalyst supports (CO oxidation). The known interactions of iron oxide surfaces with metals are described, and it is shown that the behaviour is determined by whether the metal forms a stable ternary phase with the iron oxide. Those that do not, (e.g. Au, Pt, Ag, Pd) prefer to form three-dimensional particles, while the remainder (Ni, Co, Mn, Cr, V, Cu, Ti, Zr, Sn, Li, K, Na, Ca, Rb, Cs, Mg, Ca) incorporate within the oxide lattice. The incorporation temperature scales with the heat of formation of the most stable metal oxide. A particular effort is made to underline the mechanisms responsible for the extraordinary thermal stability of isolated metal adatoms on Fe_3O_4 surfaces, and the potential application of this model system to understand single atom catalysis and sub-nano cluster catalysis is discussed. The review ends with a brief summary, and a perspective is offered including exciting lines of future research.

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