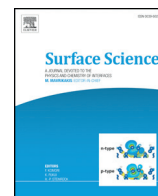




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Q1 Identification of O-rich structures on platinum(111)-supported ultrathin iron oxide films

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ABSTRACT

Using high-resolution scanning tunneling microscopy (STM) we have studied the oxidation of ultrathin FeO films grown on Pt(111), which was accomplished by atomic oxygen exposure. At the initial stage of the FeO film oxidation, we identified three distinct types of line defects, all of which form boundaries between FeO domains of opposite orientation. Two types of line defects appearing bright (*type-i*) and dark (*type-ii*) in the STM images at typical scanning parameters are “metallic”, whereas the third line defect exhibits nonmetallic behavior (*type-iii*). Atomic-scale structure models of these line defects are proposed, with *type-i* defects exhibiting 4-fold coordinated Fe atoms, *type-ii* exhibiting 2-fold coordinated O atoms, and *type-iii* exhibiting tetrahedrally coordinated Fe atoms. In addition, FeO₂ trilayer islands are formed upon oxidation, which appear at FCC-type domains of the moiré structure. At high scanning bias, distinct protrusions on the trilayer islands are observed over surface O ions, which are assigned to H adatoms. The experimental data are supported by density functional theory (DFT) calculations, in which bare and hydroxylated FeO₂ trilayer islands are compared. Finally, we compare the formation of O-rich features on continuous FeO films using atomic oxygen with the oxidation of Pt(111)-supported FeO islands accomplished by O₂ exposure.

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1. Introduction

Transition metal oxides are important in catalysis, where, among others, they are used as support materials for the actual active material – usually precious metal nanoparticles (Pt, Pd, Rh, Ru, Au) [1–4]. This simplified picture of a catalyst implies that the oxide supports would not be important for the catalytic reactivity. However, it has long been known that the supporting oxide material does influence the catalytic reactivity, especially if reducible oxides are used such as TiO₂, CeO₂ or iron oxides [5–8]. One important reason for a promotional impact of reducible oxide supports on catalysis is that O ions of the support can participate in the chemical reactions. In the so-called “Mars–Van Krevelen mechanism”, O ions of the support are consumed within the surface reactions (reduction of the oxide support), and gas phase oxygen re-oxidizes the oxide support at the end of a catalytic cycle [9].

The removal of O ions from the oxide surface lattice in its stoichiometric form is energetically often very costly and cannot occur at low

reaction temperatures [10]. In oxidation reactions at O₂-rich conditions, an alternative is that O-rich surface structures or chemisorbed oxygen species at the oxide–metal interface are involved in the surface chemistry rather than O ions from the oxide lattice [11]. Accordingly, the structural and chemical assessment of O-rich structures on oxide surfaces is essential for an improved understanding of catalytic processes occurring at O₂-rich conditions.

One of the best studied model catalyst systems that couple a reducible oxide phase to a noble metal surface is the polar FeO(111) bilayer film grown on Pt(111) [2,4,12]. This model system is of high relevance since Pt is one of the most common catalysts, for example, in three-way catalytic converters, and since iron oxide is used in a number of catalytic processes, including methanol oxidation to formaldehyde, the water–gas shift reaction, and styrene production [12]. In surface science, the study of thin films is often preferred over the study of single crystalline bulk-oxides, because the preparation of metal–oxide surfaces with defined structures and stoichiometries can be very difficult [1,2].

The FeO(111) bilayer consists of hexagonal closed packed O- and Fe-layers with the O-layer at the surface and the Fe-layer sandwiched between the surface O-layer and the Pt(111) support. Because of a misfit angle of ~0.6° between the FeO(111) film and the Pt(111) support and the lattice mismatch between the FeO lattice (~3.1 Å) and the Pt(111) substrate (2.77 Å) the FeO(111) bilayer on Pt(111) is

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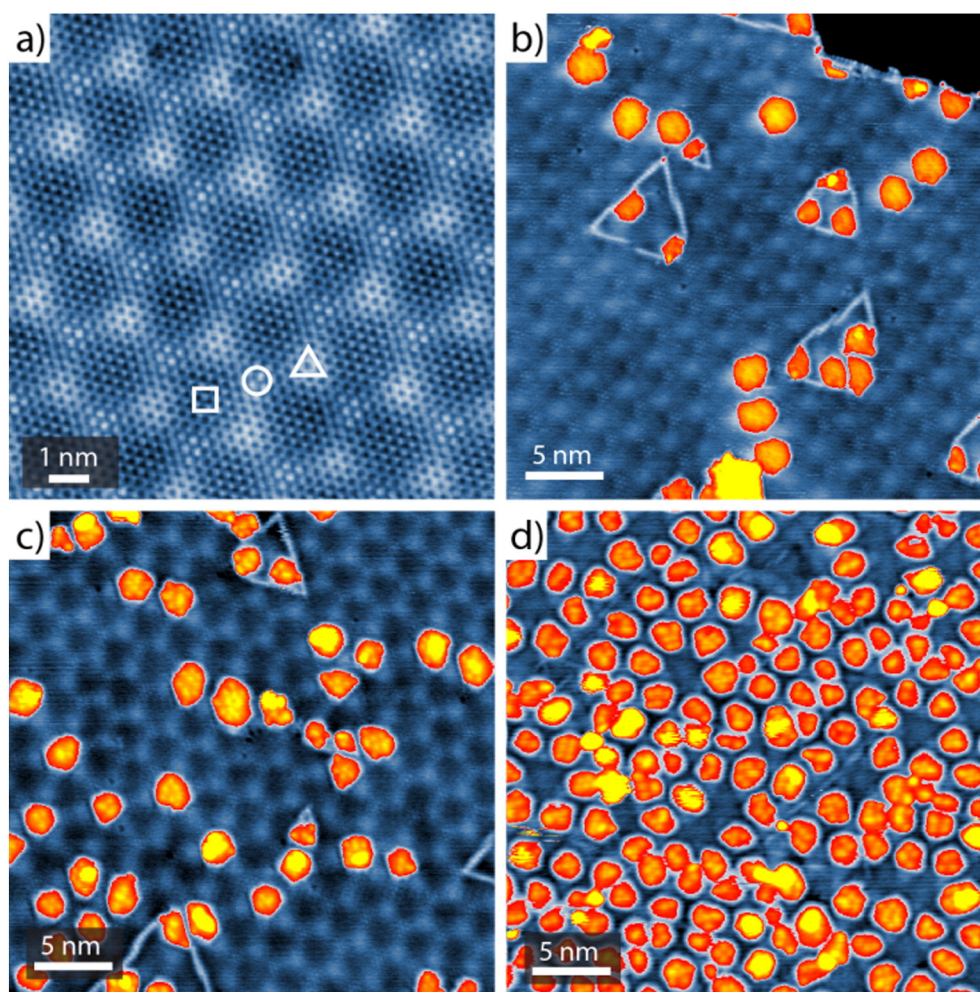


Fig. 1. a) STM image (65 mV, 3 nA) of the FeO monolayer film on Pt(111). Symbols mark the three different high-symmetry domains (\square = FCC, \circ = top, \triangle = HCP). b,c,d) STM images of the FeO film after exposure to increasing doses of atomic oxygen (O_2 background pressure set to 1×10^{-8} mbar), followed by brief annealing at 500 K. b) (0.9 V, 0.2 nA) 90 s, c) (1.0 V, 0.3 nA) 180 s, d) (2.0 V, 0.2 nA) 480 s.

77 characterized by a moiré pattern, which shows a ~ 25 Å periodicity (see
 78 Fig. 1a). The FeO(111) bilayer film on Pt(111) has been studied in great
 79 detail by means of scanning tunneling microscopy (STM) [13–20], X-ray
 80 photoelectron diffraction [20,21], density functional theory (DFT)
 81 [15–17,19,20], and a number of other surface science techniques [12].

82 A related system has been derived from the FeO bilayer films, which
 83 consists of Pt(111)-supported FeO bilayer islands [22–24]. This is a so-
 84 called “inverse catalytic model system” [4,7,25], where the precious
 85 metals are covered by ultrathin oxide patches. In contrast to continuous
 86 FeO bilayer films on Pt(111), the FeO–Pt(111) interface in these model
 87 systems is accessible, rendering them catalytically very active, for
 88 example, in low temperature CO oxidation [22]. This interesting
 89 catalytic model system allows for detailed studies of the FeO–Pt(111)
 90 interface [26], so that structure–activity relationships can be established
 91 [22,24,27].

92 Another very interesting model system derived from FeO bilayer
 93 films is FeO₂/Pt(111). This system, also denoted as O–Fe–O (FeO₂)
 94 trilayer structure, was first proposed by Sun et al. who exposed a
 95 FeO(111) bilayer film to O₂ pressures in the mbar regime at elevated
 96 temperatures [6]. The observed enhanced CO oxidation activity
 97 [compared to clean Pt(111) and nm-thick Fe₃O₄(111)] following this
 98 preparation was linked to the formation of FeO₂ islands, which are char-
 99 acterized by an O–Fe–O–Pt stacking [6,28,29]. Thus, in contrast to the
 100 FeO(111) bilayer film, the FeO₂ trilayer islands contain O atoms at the
 101 interface between the oxide film and the Pt(111) substrate. Although
 102 the “FeO₂ trilayer structure” is catalytically very active, Fu et al. reported

103 that this system is less active in low-temperature CO oxidation than Pt-
 104 supported FeO bilayer islands [30].

105 We have previously studied the evolution of O-rich structures on
 106 FeO/Pd(111) by STM and DFT [31]. Upon exposure to atomic O, the for-
 107 mation of ordered, triangular O adatom dislocation loops was observed
 108 on the Pd(111)-supported FeO bilayer [31]. We found that the sides of
 109 these triangular structures are composed of 4-fold O-coordinated Fe
 110 atoms as opposed to the original 3-fold O-coordinated Fe atoms in the
 111 stoichiometric FeO film. The identification of the O adatom dislocation
 112 loops on FeO/Pd(111) was crucial for the assignments of the edge-
 113 terminations on Pt(111)-supported FeO nanoislands (see ref. [26,27]).
 114 Upon further O exposure the O dislocation loops on FeO/Pd(111) spread
 115 in a disordered manner, before the formation of FeO₂ trilayer islands set
 116 in. However, no systematic study on the evolution of O-rich structures
 117 on FeO/Pt(111) exists yet.

118 In the present work, we study the oxidation of FeO/Pt(111) by atom-
 119 ic O exposures at temperatures between 300 and 500 K in a stepwise
 120 fashion. Three distinct types of line defects are identified, all of which
 121 form boundaries between FeO domains of opposite orientation.
 122 Atomic-scale structure models of all these line defects are proposed
 123 on the basis of STM images. At high O exposures, FeO₂ trilayer islands
 124 are formed, which were found preferentially at FCC-type domains of
 125 the moiré structure. Distinct protrusions on the trilayer islands are
 126 observed over surface O ions, which we assign to H adatoms. This
 127 assignment and the structural details of the FeO₂ trilayer islands are
 128 further addressed in our DFT modeling.

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