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Structure and properties of a model oxide-supported catalyst under redox conditions: $WO_x/\alpha\text{-}Fe_2O_3$ (0001)

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ABSTRACT

Relaxed structures and the related electronic environments of atomic monolayers and half-monolayers of tungsten with varying degrees of oxidation on the (0001) surface of hematite (α-Fe_2O_3) are modeled using first-principles density functional theory (DFT). This report focuses on the effect of nominally oxidizing and reducing chemical environments on surface structure and chemistry. By considering the position of W atoms relative to the substrate, calculated surface structures are compared to synchrotron X-ray standing wave (XSW) imaging results recently reported for this system. The question of W valence state, previously reported as nominally W^{5+} or W^{6+} in reducing or oxidizing surroundings, respectively, is addressed and discussed in light of X-ray photoelectron spectroscopy (XPS) and extended X-ray absorption fine structure (XAFS) results to clarify the relationship between valence state, oxygen coordination, and bond lengths.

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1. Introduction

Low-coverage layers of transition metals or their oxides atop oxide substrates of different compositions are of interest for various applications, most notably gas sensing and catalysis [1,2]. For oxide-supported heterogeneous catalysts, the catalytic selectivity and activity for specific reactions are defined by the composition of both the oxide substrate and the metal or metal oxide overlayer and the structure of the interface. The atomic and electronic structures of surface active sites must be well defined in order to understand the catalytic mechanism and for the rational design of reaction pathways with catalysts [3].

In previous work [4,5], density functional theory (DFT) has been combined with surface-sensitive X-ray techniques to characterize monolayer and sub-monolayer coverage vanadium oxides (VO_x) on α-Fe_2O_3 (hematite) (0001) surfaces under relevant chemical conditions. X-ray photoelectron spectroscopy (XPS) was employed to probe chemical changes when the surface was subjected to oxidizing and reducing conditions [6]. X-ray standing wave (XSW) imaging provided a sub-atomic-scale map of V positions relative to the hematite lattice under the same chemical conditions. Each of these methods revealed that chemically induced changes in the surface structure were reversible, indicating "redox reversibility", an important quality in catalytic behavior. With the use of the same experimental methodology, the structure and chemical properties of a similar heterogeneous catalyst [7], tungsten oxide (WO_x) atop the hematite (0001) surface, have recently been elucidated [8].

While XSW has provided insight on the positions of metal cations at the surface with respect to bulk cation positions, it is not possible to resolve the configuration of surface oxygen and iron atoms with the present experimental methodology. These details of surface stoichiometry and reconstruction are necessary to elucidate the chemical mechanisms underpinning catalysis and the contributions of both W and Fe, which provide acidic sites for catalytic reactions [9–11]. For example, mixed W–Fe catalysts are considered for potential heavy gas oil hydrotreatment needed for extraction of petroleum from oil sands and tars. The interactions between the two metals and with the oxide support in forming active catalytic complexes which lead to desirable activity and selectivity remain essentially unknown. In this work, DFT is employed to explore several proposed surface structures under both ideal (dry) and hydroxylated conditions. EXAFS results for 1/3 monolayer (ML) WO_x on hematite (0001) are also discussed in light of theoretical predictions based upon embedded cluster models.

Slab model DFT calculations were performed for half-ML and ML W on O- and Fe-terminated hematite (0001) surfaces. Self-consistent structural relaxations were carried out, followed by detailed density of states (DOS) calculations. After the details of the methodology are outlined, results will be presented for half-ML W coverage on O-terminated hematite (0001), revealing the consequences of varying O coordination, hydroxylation, and surface O vacancies on the surface structure and chemical properties. The effect of additional surface Fe will be discussed under the same light, as well as full ML coverage of W. After a short commentary on corrections for well-known strongly correlated electron effects in iron

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oxides, comparisons will be drawn between the presented calculations and recently published experimental results.

2. Methodology

The Vienna Ab Initio Simulation Package (VASP) was utilized to perform spin-polarized periodic slab DFT calculations with plane-wave basis sets [12–16]. The interactions between ionic core pseudopotentials and valence electrons were modeled using the projector augmented wave (PAW) method and corrected with the spin-polarized generalized gradient exchange-correlation approximation (GGA) as developed by Perdew and Wang (PW91) [17]. While PW91 and other gradient-corrected methods show systematic errors with respect to binding energy, bond lengths, and magnetic properties, they are in general an improvement over LSDA alone. Hybrid-functional methods which include an empirical mix of Hartree–Fock exchange and some GGA formulation at considerable additional computational cost can offer further improvements, for example in the classic case of NiO [18]. The so-called B3LYP hybrid version has been successfully applied to study the various crystallographic phases of bulk hematite [19]. However, in the absence of reliable parametrizations for complex oxide surfaces, the GGA/PW91 scheme was chosen for most computations. Grids for Brillouin zone integrations were generated automatically by the method of Monkhorst and Pack [20]. $4\times4\times1$ *k*-point meshes were found to be sufficient for all structural relaxations and densities of states (DOS) calculations, which showed no significant deviations from results using $6\times6\times1$ and $8\times8\times1$ *k*-point meshes. The computational methodology described above has been recently validated in studies of vanadium oxide on the hematite surface [4,5].

Periodic supercells were constructed by decorating the surface of a 1×1 (0001) hematite slab with W, O, and H atoms to represent surface structures under oxidizing or reducing chemical environments. The relaxed O-terminated hematite surface cell contains 19 atoms, as described in Refs. [4,5]. The bottom 4 atomic layers ($Fe–O_3–Fe_2–O_3$) were held rigid to enforce bulk boundary conditions, while all other atoms were allowed to relax via a quasi-Newtonian method or conjugate gradient algorithm [21]. The two symmetrically inequivalent low-energy surface cation sites, denoted as A and B, correspond to bulk-like cation positions. Fe atoms in these sites are denoted as Fe_A or Fe_B herein, and the same scheme is used for W (W_A, W_B). Placing W in either A or B constitutes 0.5 monolayer (ML) coverage; a full ML is considered to be both sites filled. The mixed-ML case corresponds to W occupying one site and Fe in the opposite site, e.g. Fe_A and W_B. For adsorbed O atoms, subscripts will indicate the surface site from which O is nearly vertically displaced, i.e. O_A and O_B; O_S denotes a crystal surface-layer atom. A further bulk octahedral site Fe_C is required to complete the labeling nomenclature; all sites are labeled in Fig. 1 of Ref. [4]. Thus the stacking sequence of the ideal O-terminated surface is $O_3–Fe_CFe_B–O_3–Fe_AFe_C–O_3–Fe_AFe_B…$

After structural relaxation, the electronic charge associated with each atom was determined using two different and complementary methods. Electron density was integrated over spherical volumes of variable radius R_S centered at atomic lattice positions, generating so-called Wigner–Seitz (WS) charges. This density was further projected onto the occupation of site-specific *s*, *p*, and *d* valence shells, allowing the calculation of the total density of states (DOS) of the surface cell and orbitally weighted partial densities of states (PDOS) for individual atoms. R_S values were chosen by adjusting empirical ionic radii so that the (typically overlapping) atomic volumes add approximately to the unit cell volume. In this work, R_S values were fixed at 1.6 Å for O, 0.9 Å for Fe and W, and 0.7 Å for H.

Bader topological charge analysis was also employed by way of the algorithm developed by Henkelman et al. [22]. This method describes atoms by partitioning space along zero flux surfaces of electron density, providing a complementary view of ionicity often substantially different from that of WS spherical volumes. Both WS and Bader schemes have proved to be useful in interpreting chemical bonding and the structure in molecules and solids. Both methods are used in the present work to compare the net charge on surface W atoms with nominal ionic values and calculated neighboring Fe charges under different chemical conditions. Detailed charge density maps were also prepared to display extended surface-related charge distributions and W – O covalency.

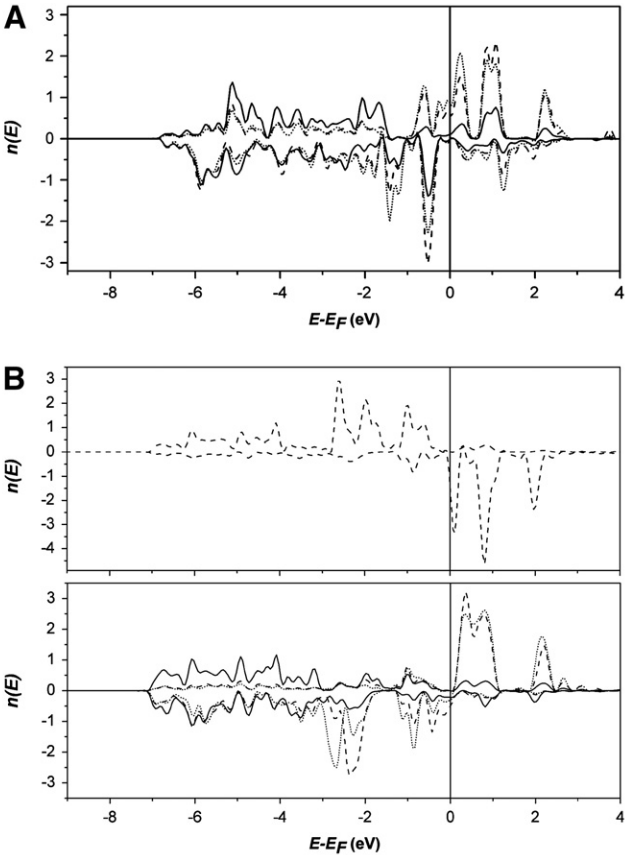

Fig. 1. (A) Surface and near-surface atoms of clean O-terminated hematite: solid line O_S, dashed Fe_C, and dotted Fe_B. Here and in following figures, $n(E)$ is the density of states for each cation or the average density of states per atom for each oxygen layer. (B) Surface and near-surface atoms of clean Fe_A-terminated hematite. Upper panel: Fe_A; lower panel: solid line O_S, dashed Fe_C, and dotted Fe_B.

In XP spectra, shifts of ~1–2 eV in core-shell energy levels are observed to indicate changes in the degree of oxidation in metals. The XP shifts of the W 4*f* core-level doublet observed by Feng et al. [8] for sub-ML $WO_x/\alpha\text{-}Fe_2O_3$ (0001) are consistent with conventional interpretations of W^{5+} and W^{6+} states. W^{4+} was not observed. Excitations of core-level states create strong localized perturbations in the ground state potential which are reflected in spectral properties, including energy level shifts and wave-function distortions. Local perturbations are not easily treated in band structure methods, however, as interference between localized holes in neighboring cells influences calculated results [23]. While large supercells can in principle resolve this problem, localized molecular cluster models offer an attractive alternative. The molecular orbital description used in this approach provides an intuitive chemical interpretation of the hole-induced atomic-state changes around the excitation site. Localized-state embedded cluster methods [24] were employed herein for analyzing XPS spectra. Several cluster models, based on the ground state periodic structures, were studied.

Spectroscopic transition energies, which are rigorously differences in *total energy* between initial and final states, can be quantitatively approximated in the Slater transition state (TS) scheme as the differences between *one-electron energies*, defined by the TS Hamiltonian [25]. In its simplest form the TS Hamiltonian is derived by an expansion of the total energy in a Taylor series of the orbital occupation numbers as $H^* = (H_i + H_f)/2$, i.e., the average of initial and final state Hamiltonians.

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