



Periodic density functional theory study of maghemite (001) surface. Structure and electronic properties



Yenner L. Bentarcut^{a,b}, Mónica Calatayud^c, Jaime Klapp^{d,e}, Fernando Ruetter^{b,*}

^a Departamento de Química, Instituto Universitario de Tecnología, Dr. Federico Rivero Palacio, Apartado 401047, Caracas 1040-A, Venezuela

^b Centro de Química, Instituto Venezolano de Investigaciones Científicas (IVIC), Apartado 21827, Caracas 1020, Venezuela

^c Sorbonne Université, CNRS, Laboratoire de Chimie Théorique, LCT, Paris F. 75005, France

^d Departamento de Física, Instituto Nacional de Investigaciones Nucleares (ININ), Carretera México-Toluca km. 36.5, La Marquesa, Ocoyoacac, Estado de México 52750, México

^e Abacus-Laboratorio de Matemática Aplicada y Cómputo de Alto Rendimiento, Departamento de Matemáticas, CINVESTAV-IPN, Carretera México-Toluca Km 38.5, La Marquesa, Ocoyoacac, Estado de México, 52740 México

ARTICLE INFO

Keywords:

Maghemite
Surface modeling
DFT-U
Electronic properties
 γ -Fe₂O₃(001)

ABSTRACT

The structure of the iron oxide γ -Fe₂O₃ surfaces along (001) direction has been modeled for the first time using periodic DFT. Four different types of surfaces were analyzed depending on the upper layer composition (presence of tetrahedral or octahedral Fe) and the presence of iron vacancy locations. The inclusion of a Hubbard (DFT + U) correction allows a good agreement between calculated and experimental bulk properties. Relaxation of surface layers results in important surface reconstructions, electronic charge transfer with respect to the bulk, and a decrease in the dipole moment. Surfaces with tetrahedral Fe atoms on the top layer resulted to be the most stable ones. An almost linear correlation between the work function and the electronic charge transfer to O atoms was found. An analysis of the density of states shows that the Fermi level in tetrahedral Fe-terminated surfaces is far from the valence band whereas the reverse occurs with octahedral Fe-terminated atoms. The tetrahedral Fe-terminated surface has a more basic character than the octahedral ones. In addition, the presence of a subsurface Fe vacancy stabilizes the system and seems to be adequate for bond activation by electron transfer from the surface to the adsorbate, such as H₂.

1. Introduction

The catalysis research for many reactions of high importance in chemical and material industries involves the use of noble metal catalysts, such as palladium, iridium, platinum, rhodium, gold, and ruthenium [1–8]. However, the high cost and limited availability of these precious metals have spurred activity of research for new catalytic materials in order to generate other alternatives. In this sense, the use of first-row transition metal compounds as substitutes are of great interest, particularly for large-scale applications [9–13].

Iron oxide compounds are widely applied in many technological fields: catalysis [10,11,14–25], magnetic materials on nanoscale [19], nanocomposite production [26–28], carbon fuel cell [10,29], magnetic drug delivery [27,30,31], pollutant remover [32,33], etc. Recently, solid catalysts, composed of γ -Fe₂O₃ nanoparticles supported on a carbonaceous surface, have been synthesized with excellent catalytic properties for nitroarenes reduction [14]. Maghemite (γ -Fe₂O₃) exhibits ferrimagnetic ordering with a net magnetic moment (1.25 μ_B /iron

atom) in contrast with the antiferromagnetic hematite (α -Fe₂O₃), and in addition, it is the second most stable polymorph iron oxide phase [34]. This material is commonly used, due to its magnetic properties, in areas such as biological applications and biomedicine; however, several studies also show an important role as a catalyst in various chemical processes [11,14–16,19,25].

As mentioned above, iron oxide has been prepared as a catalyst with special conversion and high selectivity for nitroarenes hydrogenation, even under comparably mild conditions, similar to noble metal catalysts for hydrogenation of substituted aromatics [35]. This finding is in line with recent research showing that cerium oxides are able to activate H₂ in the absence of noble metals [36–38].

The nanostructure of Fe₂O₃ has been reported by Jagadeesh et al. [14] who determined small size particles ($d \leq 5$ nm) with an iron oxide phase corresponding to maghemite, using transmission electron microscopy (TEM), Mössbauer spectroscopy, and electron paramagnetic resonance (EPR). In another study, Mou et al. [17] synthesized rod-shaped Fe₂O₃ as an efficient catalyst for the selective reduction of

* Corresponding author.

E-mail address: fruetter@gmail.com (F. Ruetter).

<https://doi.org/10.1016/j.susc.2018.06.005>

Received 9 February 2018; Received in revised form 30 May 2018; Accepted 13 June 2018

Available online 18 June 2018

0039-6028/ © 2018 Elsevier B.V. All rights reserved.

nitrogen oxide to ammonia. Their results from XRD, SEM and TEM observations revealed that the γ -Fe₂O₃ nanoparticles have an average diameter of 40 nm and a mean length of 400 nm. These authors also found that these nanorods have (110) as end planes, and (1 $\bar{1}$ 0) and (001) as side planes. Further investigations in similar systems have been performed by Sharifi et al. [19] on the formation of nitrogen-doped graphene nanoscrolls by adsorption of magnetic γ -Fe₂O₃ nanoparticles. They proposed a strong adsorption of maghemite nanoparticles at nitrogen defects in the graphene lattice and their mutual magnetic interaction. In this sense, Qiu et al. [39] developed a highly efficient oxygen reduction catalyst based on these compounds to replace the relatively expensive platinum-loaded carbon counterparts. The catalyst nature was a nanoconfined maghemite in a nitrogen-doped graphene that surpasses the performance of the equivalent commercial PtC, in terms of a higher reduction potential and a significantly lower peroxide formation. In the same manner, Medisetti et al. [18] developed a nano- γ -Fe₂O₃ catalyst for *N-tert*-butoxycarbonylation of amines in water that is efficient, reusable, and green. They analyzed the morphology and size of the nano- γ -Fe₂O₃ particles by using XRD, SEM, and TEM techniques and found a nanocrystalline nature with a grain diameter of 15 nm. A theoretical study of γ -Fe₂O₃ surfaces is relevant to understand the catalytic properties of this material.

The maghemite crystal structure has been the subject of controversy in the last years. A work by Greaves [40] using powder neutron diffraction proposed a tetragonal P4₃2₁2 symmetry for maghemite. On the contrary, Guivar et al. [41] reported that the γ -Fe₂O₃ XRD diffractogram fits very well with the cubic symmetry (space group P4₃32). On the other hand, Shmakov et al. [42] using powder diffraction data and high-resolution electron microscopy show that the maghemite structure possesses cubic symmetry (space group P4₃32), whereas the ordered distribution of the cation vacancies in the octahedral positions results in the formation of the tetragonal superlattice (space group P4₁2₁2). Moreover, theoretical calculations by Guo and Barnard [43] found that, although the long-range ordering of vacancies changes the symmetry of the lattice, the elasticity tensor seems to be independent of the symmetry change. It means, there is a small difference in the elastic properties of tetragonal and cubic symmetries. Serna and Morales [44] reported that the spinel structure of γ -Fe₂O₃ contains cation vacancies, which can be ordered (tetragonal superstructure), partially ordered (cubic superstructure), or completely disordered. In addition, Prado et al. [45] showed by using XRD, TEM, and XPS that small maghemite nanoparticles have a cubic structure. Similar results have been also reported by Sharifi et al. [19], Chernyshova et al. [46] and Wu et al. [47].

Few theoretical studies have been performed to model the maghemite crystal. A pioneer work was carried out by Grau-Crespo et al. [34] by using a DFT method with Hubbard (DFT-U) correction. They found the tetragonal P4₁2₁2 configuration as the most stable. On the other hand, calculations by Guo and Barnard [43], using a similar level of theory and employing the tetragonal P4₃2₁2 symmetry proposed by Greaves [40], reproduced the correct magnetic ordering for several oxides, predicting that a ferrimagnetic state has a lower formation energy than non-magnetic and ferromagnetic states.

Scarce experimental and theoretical works have been performed on maghemite surfaces. Bowker et al. [48] studied the surface structure of γ -Fe₂O₃(111) using a range of surface techniques. They found two different surface structures, depending upon surface preparation techniques. For example, surface sputtering followed by annealing in a vacuum produced a reduced surface characterized by a (2 × 2) LEED pattern, whereas the same treatment in 1 × 10⁻⁶ mbar oxygen produced a surface characterized by a ($\sqrt{3}$ × $\sqrt{3}$)-R30° LEED pattern. In another experimental study, Chamber and Joyce [49] analyzed surface termination, composition, and reconstruction of Fe₃O₄(001) and γ -Fe₂O₃(001) surfaces. They reported that γ -Fe₂O₃ (001) surfaces are reactive because they readily chemisorb oxygen or hydroxyl, depending on the method of preparation.

Theoretical calculations with periodic DFT are nowadays a common procedure to understand catalytic reactions [50–53]. Nevertheless, theoretical modeling for γ -Fe₂O₃ surfaces, as far as we know, has not been performed. In this study, the properties of γ -Fe₂O₃ (100) terminated surfaces are analyzed as regards their geometry, energetics, and electronic structure using a periodic DFT method. This work is organized as follows. A brief description of the computational method, calculation parameters, bulk model, and the selection of crystal surface slab models are presented in the next section. In addition, a validation of the methodology and the crystal model is also discussed by comparison with experimental crystal bulk properties. In the Section of Results and Discussion, calculations of selected surfaces were analyzed as regards Fe-vacancy locations (on top vs in subsurface layers Surface relaxation by optimization layer by layer was studied. Graphical descriptions were displayed for evaluating surface reconstruction. In addition, several properties were calculated, such as cleavage energy, relaxation energy, surface energy, work function, atom coordinate changes, and charge density, to fully characterize the surfaces. Projected density of states were also performed to identify the Fermi level, atomic orbital contributions, band gap, valence band, and the conduction band; prediction of STM images for the most stable surface was also presented. Finally, the last section describes the most relevant results and future work by considering catalytic properties.

2. Computational details and models

2.1. Computational method

Our calculations were carried out by using a spin-polarized density functional theory (DFT-U), where U is the Hubbard correction [54], with the exchange and correlation functional PBE [55], as implemented in Quantum Espresso [56]. The effect of the core electrons was simulated by an ultrasoft pseudopotential [57], with nonlinear core correction and scalar relativistic approach [58]. The valence electrons were expanded in a plane-wave basis, that has been used successfully to obtain accurate structural and electronic properties of transition metal oxides including iron oxides [59]. A kinetic energy cutoff 50 Ry for the wavefunction and 800 Ry for the charge density was selected. For achieving an accurate self-consistent electronic convergence, the Brillouin zone sampling was an optimized k-point grid of 6 × 6 × 6 for the bulk and a 4 × 4 × 1 for surfaces models. An 8 × 8 × 1 grid with additionally a smearing of 0.005 Ry to the orbital occupation was used for post-processing calculations. The convergence threshold for self-consistency was set to 1 × 10⁻⁸ Ry and for structural optimization the total energy threshold was 1 × 10⁻⁴ Ry, considering that forces for each atom have a value smaller than 0.02 eV/Å.

To correct the excessive delocalization of electrons characteristic of transition metal oxides, the Hubbard correction was used for the 3d levels of the iron atom. This correction has been reported for magnetite, maghemite, hematite, and goethite to be between 1.0 eV and 6.0 eV [43]. In this work, it was optimized (4.1 eV) to obtain a good match with the experimental band gap, lattice parameters, the previously calculated density of states, Fe–O bond distances, and magnetic moments, as it is shown below. The Löwdin analysis [60] was employed to estimate the partial atomic charges, and the software Vesta [61] was used for depicting bulk and surface models. A dipole correction is employed by using the method for surface supercell proposed by Bengtsson [62]. The simulated STM images were carried out with XCrySDen [59].

The STM images were simulated according to the Tersoff–Hamann approach [63] where the STM tip was replaced with a point probe. For a positive (negative) bias voltage, the STM images provide information for unoccupied (occupied) states, respectively. The tunneling current between the surface and the probe in the STM experiment is proportional to the surface local density of the states (LDOS) integrated around the Fermi energy, and the image represents a contour map of

Download English Version:

<https://daneshyari.com/en/article/7844661>

Download Persian Version:

<https://daneshyari.com/article/7844661>

[Daneshyari.com](https://daneshyari.com)