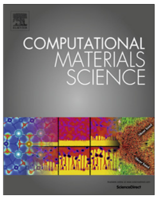
Computational Materials Science 127 (2017) 110–120

Contents lists available at ScienceDirect

Computational Materials Science

journal homepage: www.elsevier.com/locate/commatsci



Adsorption of As(III) and As(V) compounds on Fe_3O_4(0 0 1) surfaces: A first principle study

Samuel E. Baltazar [a,*], Aldo H. Romero [b], Marcelo Salgado [a,c]

[a] Departamento de Física and CEDENNA, Universidad de Santiago de Chile, USACH, Av. Ecuador 3493, Santiago 9170124, Chile
[b] Physics and Astronomy Department, West Virginia University, Morgantown 26506, WV, USA
[c] Fraunhofer Chile Research, Center for Solar Energy Technologies, Vicuña Mackenna 4860, Santiago 7820436, Chile

ARTICLE INFO

Article history:
Received 7 June 2016
Received in revised form 18 October 2016
Accepted 25 October 2016

Keywords:
Arsenic
Iron oxides
Adsorption
Density functional theory

ABSTRACT

The adsorption of arsenic species on magnetite has been studied by first principles calculations. From the considered anionic species, a higher adsorption energy was found for the complexation of Fe_3O_4(0 0 1) with As(III) being 1.3 eV higher than the adsorption energy for As(V). In the case of As(III), a large partial band charge density was found, which was associated to the O—Fe bond formation, while more delocalized electron density was found in the adsorption of As(V) subspecies, with the formation of two Fe—O bonds. A comparison with sorption of neutral arsenic atoms and O_2 molecule was also considered. As (V) is mainly adsorbed on the surface with a double O—Fe bond formation, similar to the case of O_2 in the most stable configuration.

1. Introduction

In the last few years, the presence of metalloids and heavy metals in aqueous sources has been a major concern and it is going to be even more important as the water consumption increases. In this context, several pollutants found via natural processes such methylated arsenicals, or heavy metals (Pb, Cd, Cr, etc.) from several anthropogenic activities have been investigated [1–4]. Arsenic is a metalloid which can be found in contaminated water in two different oxidation states: arsenite As(III) and arsenate As(V) and with different protonated subspecies going from $AsO(OH)_3$ to AsO_4^{3-} $^{-}$ and $As(OH)_3$ to AsO_3^{3-}. These subspecies are controlled by the acidic conditions present in water from which can be related to the pH and pK values. These arsenic species are considered as carcinogen agents by the World Health Organization and their ingestion are considered treats to the human health [5], as for example, in the disruption of the production of adenosine triphosphate, which is the responsible of energy transportation in cells [6]. The high toxicity of the pollutants has demanded new alternatives to purify water resources. In particular, a great attention has been put into the application of iron nanoparticles to capture these arsenic compounds [7,8]. The atomic nanoparticle surface reconstruction, obtained from its natural oxidation process, is observed at different pH conditions. These conditions promote the nucleation of iron oxides polycrystals on the surface of the nanoparticles, which happen to be related to their sorption capabilities [9]. This surface reconstruction has been experimentally characterized by considering several external conditions [10]. The obtained results show the presence of magnetite, hematite, lepidocrocite and other iron oxyhydroxide structures at the nanoparticle surface. In the case of magnetite, it was demonstrated that this compound grows on the nanoparticle with a (0 0 1) orientation which is the dominant orientation, even though, in small rate, it is possible to find the (1 1 1) and (1 1 0) orientations [11–13].

The presence of different Fe oxidation states has been directly related to the sorption capacity of the nanoparticles [1,7,9,14,15] as it interacts with different metallic atoms (Cr, Cu, Pb, etc.) or metalloids such as Arsenic molecular species. The interaction between arsenic molecules with iron oxides and oxy(hydr)oxides surfaces leads to the formation of inner-sphere complexes during the adsorption process and eventually the formation of covalent bonds between the adsorbed species and the surface atoms.

In this work, we study the interaction of arsenic complexes in contact with iron oxide surfaces at the atomic scale. Even though the hydrated iron oxide surface is a more realistic condition in the sorption process, an ideal surface can be suitable to study specific interactions between arsenic species and the magnetite.

Our results clarify how the different associated oxidation states of the adsorbed molecules are chemisorbed by iron nanoparticles, which is a relevant process for the pollutant problem as previously discussed. A detailed analysis of the structural changes due to the interaction between arsenic compounds and the Fe_3O_4 surface is

---

* Corresponding author.
E-mail addresses: samuel.baltazar@usach.cl, samuel.baltazar@gmail.com (S.E. Baltazar).

http://dx.doi.org/10.1016/j.commatsci.2016.10.029

presented. Electronic and magnetic properties such as charge density and magnetic moments are reported as a function of different arsenic complexes. We have selected only two different As complexes with two different oxidation states as they are the most common when As is present as water pollutant, as it has been concluded in experimental measurements [16–18].

2. Methodology

2.1. Computational methods

In order to calculate the total energy and simulate the structural optimization of pristine magnetite and the adsorption of different molecules we have performed first principle calculations based on the density functional theory (DFT) [19] within the generalized gradient approximation (GGA) and with the exchange-correlation functional proposed by Perdew et al. and also known as PBE [20]. DFT has been extensively used to study iron oxides crystals and surfaces [13,21] as well as molecular adsorption. In general, good agreement with experimental results have been reported [22,23]. The numerical simulations as well as the electronic description are obtained by using an expansion of the Kohn-Sham orbitals with the augmented wave based method (PAW) as implemented in the VASP package [24].

Although spin-polarized system has been considered in our calculations, spin-orbit coupling contribution was neglected, mainly because it is expected that changes in the electronic properties are small with respect to it. In this context, initial magnetic moments were defined following the ferrimagnetic configuration associated to magnetite, which means that Fe atoms occupy octahedral and tetrahedral sites with opposite magnetic moments, as it has been recognized by interpreting the experimental results for bulk magnetite [25–27]. Due to the strong correlation present in the localized d-states of Fe, standard LDA and GGA functionals are unable to describe correctly the electronic configuration of these systems. Therefore, we have considered the DFT + U method to correct the lack of strong correlation in these functionals by following the approach given by Dudarev et al. [28]. This method introduces a correction to the used functional by adding a term obtained from the Hubbard Hamiltonian, where the on-site Coulomb repulsion, U, was set 4.5 eV and the exchange parameter, J, was set to 0.89 eV. Both parameters have been already used in the literature with good agreement in structural and electronic properties of iron oxides between theoretical predictions and experiments [22,29]. In order to consider possible effects of van der Waals corrections in the sorption study, due to fluctuations in charge density of the surface, we have added the correction optPBE-vdW of a non-local correlation functional proposed by Klimes et al. [30]. The energy cutoff for the plane wave expansion part of the PAW functions was set to 400 eV, where well converged results were obtained (0.01 meV per unit cell for the energy and 0.001 eV/Angs for interatomic forces). The forces and stresses were minimized by following the conjugated gradient algorithm. In order to have a good representation of the Kohn-Sham orbitals in the reciprocal space, our simulations considered a Monkhorst-Pack grid with a grid of 8 × 8 × 1 for all surface calculations. A empty space of 14 Angs was considered to avoid periodic interactions of the considered slab geometry.

3. Results

3.1. Fe_3O_4 bulk structure

In order to validate the parameters considered in our study, we started our work with the bulk structure of Fe_3O_4. The ground state of this material corresponds to an inverse spinel structure with space group *Fd3m*, where the 32 oxygen anions crystallize in a close-packed fcc lattice and the Fe atoms are located at the interstitial sites grouped in 8 Fe^{3+} (tetrahedral sites) and 16 Fe^{2+} (octahedral sites) ions. The obtained interatomic distances were d$(O{-}Fe^{tet}) = 2.056$ Angs and d$(O{-}Fe^{oct}) = 1.892$ Angs, while the octahedral planes are separated by 2.09 Angs and the optimized lattice parameter was $a = 8.934$ Angs, which are consistent with the experimental results [31]. The magnetic moments associated to tetrahedral and octahedral sites are −4.02 and 3.92 respectively and are depicted as blue arrows in Fig. 1A, which result on slightly higher values than experimental results [32]. The calculated density of states (DOS) (see Fig. 1B) shows a half-metallic behavior due to the insulating behavior of the majority spin band (black line) and the metallic behavior due to the presence of the minority spin band (red line) around the Fermi level E_F, which is in agreement to the results previously reported by Arras et al. [33].

3.2. Fe_3O_4(0 0 1) surface

The Fe_3O_4 structure mainly grows, at natural conditions, along the (1 1 1) and (0 0 1) directions, being (1 1 0) a less common orientation of the structure [11]. Theoretical studies have suggested that Fe_3O_4(0 0 1) (see Fig. 2) is thermodynamically more favorable than other orientations [12,13]. This orientation can be identified as a stacking sequence of alternating layers of octahedral (odd L in Fig. 2a) and tetrahedral (even L in Fig. 2a) coordination sites. From the (0 0 1) orientation, the octahedral Fe termination is energetically more favorable than the tetrahedrally coordinated Fe [12,34]. In our work we have considered a system in a simulation unit with lateral dimension of 8.39 × 8.39 Angs, while the perpendicular axis was set up to 22.39 Angs, given an actual slab dimension of 8.5 Angs and a periodic image distance of 14 Angs vacuum, to avoid spurious slab interactions. Eight layers were considered to build the simulated slab as depicted in Fig. 2a, where the first 4 layers were allowed to fully geometrically relax and the last 4 were kept fixed during the geometry optimization process to simulate the bulk behavior. Therefore, we are assuming that the surface relaxation occurs within the first top layers, a fair assumption which has proven to be quite accurate in similar systems [13,35]. In this context, a $(\sqrt{2} \times \sqrt{2})R45^\circ$ reconstruction of Fe_3O_4(0 0 1) has been obtained after the surface relaxation (see Fig. 2b and c), in agreement to experimental results [36]. This has been attributed to a Jahn-Teller distortion effect from the different *d*-orbital occupation [12]. On the top layer there is a Fe atom with two O atoms bonds at 1.99 Angs and two O atoms at 2.01 Angs, which shows a nonequivalent distortion with respect to the 2.06 Angs obtained in the bulk structure. Fig. 2d shows the projected DOS of the relaxed surface, depicting only the contributions of the relaxed layers, where majority states near the Fermi level were associated to the unrelaxed and fixed atoms of the last layers (L7 and L8) and identified as orange lines in the bandstructure (see Fig. 2e), therefore their contribution can be separated of the sorption analysis. These results are in agreement with the study of stability and electronic structure reported by Fonin et al. [36].

3.3. O_2 molecule on Fe_3O_4(0 0 1) surface

The adsorption of O_2 molecules on Fe_3O_4(0 0 1) surface under vacuum conditions was considered. Two different initial configurations were taken into account: (i) oxygen atom on top of the surface Fe atom and in the other O between of two Fe atoms, and (ii) an oxygen dimer sits between two Fe atoms. The most energetically favorable configuration was obtained when the two O atoms were bounded to the octahedral Fe atoms at a distance d(Fe—O) = 1.983 Angs (see Fig. 3c), while the O—O inter molecular distance