DFT study of electronic and redox properties of TiO₂ supported on olivine for modelling regolith on Moon and Mars conditions

Elizabeth Escamilla-Roa^{a,*}, Maria-Paz Zorzano^{b,a}, Javier Martin-Torres^{a,c},
Alfonso Hernández-Laguna^c, C. Ignacio Sainz-Díaz^c

^a Department of Computer Science, Electrical and Space Engineering, Luleå University of Technology, 97187, Luleå, Sweden

^b Centro de Astrobiología (INTA-CSIC), Torrejón de Ardoz, Madrid, Spain

^c Instituto Andaluz de Ciencias de la Tierra (CSIC-UGR), Av. de las Palmeras 4, 18100, Granada, Spain

ARTICLE INFO

Keywords:

TiO₂ regolith
Surfaces forsterite
Olivine
Anatase
Adsorption process
Chemisorption
Physisorption
Density of States (DOS)
Redox process
Density Functional Theory (DFT)

ABSTRACT

Titanium dioxide (TiO₂) is one of the most studied oxides in photocatalysis, due to its electronic structure and its wide variety of applications, such as gas sensors and biomaterials, and especially in methane-reforming catalysis. Titanium dioxide and olivine have been detected both on Mars and our Moon. It has been postulated that on Mars photocatalytic processes may be relevant for atmospheric methane fluctuation, radicals and perchlorate productions etc. However, to date no investigation has been devoted to modelling the properties of TiO₂ adsorbed on olivine surface.

The goal of this study is to investigate at atomic level with electronic structure calculations based on the Density Functional Theory (DFT), the atomic interactions that take place during the adsorption processes for formation of a TiO regolith. These models are formed with different titanium oxide films adsorbed on olivine (forsterite) surface, one of the most common minerals in Universe, Earth, Mars, cometary and interstellar dust. We propose three regolith models to simulate the principal phases of titanium oxide (TiO, Ti₂O₃ and TiO₂). The models show different adsorption processes *i.e.* physisorption and chemisorption. Our results suggest that the TiO is the most reactive phase and produces a strong exothermic effect. Besides, we have detailed, from a theoretical point of view, the effect that has the adsorption process in the electronic properties such as electronic density of states (DOS) and oxide reduction process (redox). This theoretical study can be important to understand the formation of new materials that can be used as support in the catalytic processes that occur in the Earth, Mars and Moon. Also, it may be important to interpret the present day photochemistry and interaction of regolith and airborne aerosols in the atmosphere on Mars or to define possible catalytic reactions of the volatiles captured on the Moon regolith.

1. Introduction

Titanium dioxide (TiO₂) is one of the most studied oxides due to its wide variety of Earth applications in catalysis and photocatalysis (Diebold, 2003; Linsebigler et al., 1995; Rajh et al., 2004). This solid has been also detected in other planets of the Solar System such as Mars at concentrations of up to 1.2 wt% (Arvidson et al., 2008; Bridges et al., 2015; Edwards et al., 2017; Hurowitz et al., 2017) and even in our Moon (Elphic et al., 2002) where it can reach surface concentrations up to 10–15 wt%, as well as at low concentrations on space micrometeors (Elphic et al., 2002; Gounelle et al., 2005; Lasue et al., 2018; Noguchi et al., 2011; Peters et al., 2008). The polymorphic phases of Ti dioxide are

anatase, rutile and brookite (Grant, 1959); the former one is of paramount importance as nano-material since it exhibits higher reactivity in many cases (Diebold, 2003; Linsebigler et al., 1995). Moreover, for sizes up to ~14 nm, nano-crystals appear to prefer the meta-stable anatase rather than the rutile phase. The (001) anatase surface is the minority surface in the equilibrium shape and was found to be especially reactive (Barnard and Zapol, 2004; Barnard et al., 2005).

Titanium dioxide is one of the most effective supports for low-temperature CO oxidation (Yan et al., 2004). The catalytic activities of this solid are important for the process of carbon dioxide reforming to methane (Bradford and Vannice, 1999; Wang et al., 1996). This process also has important environmental implications because both methane

* Corresponding author.

E-mail address: eliesc@ltu.se (E. Escamilla-Roa).

<https://doi.org/10.1016/j.pss.2019.104760>

Received 20 November 2018; Received in revised form 25 September 2019; Accepted 26 September 2019

Available online 28 September 2019

0032-0633/© 2019 Elsevier Ltd. All rights reserved.

Fig. 1. (a) Pristine non-dipolar (100) surfaces of forsterite. The Mg sites with different coordination on surfaces are indicated as 4-fold (4f, 4f on top) and 3-fold (3f) and some Mg and O atoms of the top surface are labelling with their numbers. Films of titanium oxide taken from (b) (100) anatase, (c) (100) Ti₂O₃, and (d) (001) anatase surfaces. The O, Ti, Si and Mg atoms are displayed as red, grey, yellow and green colour, respectively. This style is extended to the rest of figures. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

and CO₂ are greenhouse gases (Kim et al., 1994; Zhang and Verykios, 1996). There are experimental evidences that indicate that TiO₂ is a good support in the carbon dioxide photoreduction as a photocatalysts (Do et al., 2016).

The interaction of TiO₂ with stellar UV and atmospheres or volatiles in the space environment has been to date poorly investigated but it may have very important implications on the composition of atmospheres or on the photocatalytic transformation of compounds. For instance, it has been recently argued that carbon dioxide in Martian and other planetary atmospheres can be abiotically converted into a mixture of methane and carbon monoxide by ‘methanogenesis’ on porous mineral of photoactive surfaces (Civiš et al., 2017).

Interestingly, after more than 6 years of operation on Mars, the NASA Curiosity rover has demonstrated through in-situ observations that CH₄ is detected with a mean value of 0.41 ± 0.16 parts per billion by volume (ppbv) and have exhibited a strong seasonal variation (0.24–0.65 ppbv) that has repeated over consecutive years (Webster et al., 2018). The large seasonal variation in the background is also complemented with the occurrence of higher concentration temporary spikes of: first peaks of about 7 ppbv that appeared in 2013, on four occasions over a period of two months (Webster et al., 2015), and second, just recently in 2019, the highest level of methane ever detected in the atmosphere at Mars’s surface reaching a concentration of 21 ppb (Witze, 2019). The appearance and disappearance of methane on Mars remains unexplained with the present photochemical models.

Previous researches in photocatalytic properties of minerals on Mars have been focused on hematite, where it was shown that the formation of methane and other compounds from carbon dioxide and liquid water in presence of hematite could be induced by UV irradiation (Bartoszek et al., 2011). Nevertheless, a photocatalytic process of TiO₂ has been also reported through the reduction of atmospheric nitrogen to ammonia upon irradiation of rutile doped with 0.2% Fe₂O₃ (Schrauzer and Guth, 1977). The photocatalytic activity of TiO₂ can be increased by coupling semiconductors of different energy levels, or doping with metals, or non-metals (Do et al., 2016). In particular, taking as example a Martian regolith, in the Martian soil there are a great variety of minerals such as olivine, sulphate and phyllosilicate and also basalt (Peters et al., 2008). Basalt can be formed by MgO, CaO, Fe₂O₃, TiO₂, Al₂O₃, and SiO₂, and it has been recently used as a substrate mineral to adsorb carbon dioxide (Do et al., 2016). Several Mars orbital observations and surface missions have detected regoliths. Regoliths can be described as a fine-grained cohesion, that contains small rocky fragments (Peters et al., 2008) and is produced by several phenomena such as erosion, water, lava, and chemical weathering by fluids and oxidants. The Pathfinder mission described regoliths as a combination of bright red fine-grained materials that form deposits with rocks (Moore et al., 1999). However the Mars Exploration Rover (MER) Spirit found regoliths formed of basaltic sand grains in the floor of Gusev crater (Greeley et al., 2004; Herkenhoff et al., 2004).

Therefore a fundamental understanding of the properties of regoliths

Table 1Geometrical parameters (Å) and Mulliken charges (Mg, O and Ti atoms) of TiO₂/Ti₂O₃ adsorbed onto non-dipolar (100) forsterite surface.

Structure	Atom	Bonded	^{a,c} Coor. initial	^{b,c} Coor. final	^c Dist (Å)	^d Char.	Atom	Bond Os-Ti	^c Dis(Å)	^d Char.	Atom	^d Char.
Pristine	Mg ₂₅		4f	4f		1.01	O ₈			-1.00	Ti ₁	-
	Mg ₃₀		4f	4f		1.01	O ₁₃			-1.00	Ti ₂	-
	Mg ₄₈		3f	3f		1.10	O ₁₀₃			-0.84	Ti ₃	-
	Mg ₆₈		4f*	4f*		1.11	O ₄₅			-0.87	Ti ₄	-
	Mg ₉₅		4f	4f		1.01	O ₇₈			-1.00		
	Mg ₁₀₀		4f	4f		1.01	O ₈₃			-1.00		
	Mg ₁₁₈		3f	3f								
	Mg ₁₃₈		4f*	4f*								
ana_100 (TiO₂)	Mg ₂₅	^f Mg-O _{Tib}	4f	3f	2.04	1.19	O ₁₃	^b O _s -Ti	1.94	-0.98	Ti ₁	1.20
	Mg ₃₀	^g Mg-O _{Ti}	4f	4f	2.08	1.11	O ₁₀₃	SiO _s -Ti	1.87	-0.84	Ti ₂	1.39
	Mg ₄₈	^g Mg-O _{Ti}	3f	4f	2.03	1.16					Ti ₃	1.38
	Mg ₆₈		4f*	3f		1.23					Ti ₄	1.39
	Mg ₉₅		4f	4f		1.07					Ti ₅	1.25
	Mg ₁₀₀	^f Mg-O _{Tib}	4f	4f	1.99	1.10					Ti ₆	1.40
ana_001 (TiO)	reconstruction		4f	3f		0.48	O ₈	ⁱ O _s -Ti _b	1.96	-0.91	T ₁	1.09
	reconstruction		4f	3f		0.52	O ₁₃	ⁱ O _s -Ti _b	2.02	-0.90	Ti ₂	0.61
		^g Mg-O _{Ti}	3f	4f	2.16	1.18	O ₄₅	ⁱ Si-O _s Ti _b	1.92	-0.89	Ti ₃	1.09
			4f*	2f		0.50	O ₃₃	ⁱ O _s -Ti _b	1.92	-0.91	Ti ₄	0.61
	reconstruction		4f	3f		0.48	O ₇₈	ⁱ O _s -Ti _b	1.96	-0.91		
	reconstruction		4f	3f		0.52	O ₈₈	ⁱ O _s -Ti _b	2.02	-0.90		
		^g Mg-O _{Ti}	3f	4f	2.16	1.18	O ₁₀₃	ⁱ O _s -Ti	1.92	-0.91		
			4f*	2f		0.50	O ₁₁₅	ⁱ SiO _s -Ti	1.92	-0.89		
Ti₂O₃_100	reconstruction		4f	3f		0.54	O ₈	^b O _s -Ti	1.95	-0.96	Ti ₁	1.28
	reconstruction		4f	3f		0.56	O ₃₃	ⁱ O _s -Ti _b	1.86	-0.79	Ti ₂	0.89
		^f Mg-O _{Tib}	3f	5f	2.13	1.19	O ₄₅	ⁱ O _s -Ti _b	1.86	-0.89	Ti ₃	0.99
			4f*	4f*			O ₇₈	^b O _s -Ti	1.95	-0.96	Ti ₄	1.33
	reconstruction		4f	3f		0.54	O ₁₀₃	ⁱ O _s -Ti _b	1.89	-0.79	Ti ₅	1.28
	reconstruction		4f	3f		0.56	O ₁₁₅	ⁱ O _s -Ti _b	1.86	-0.89	Ti ₆	0.89
		^f Mg-O _{Tib}	3f	5f	2.13	1.19					Ti ₇	0.10
											Ti ₈	1.33

^a Coor. initial = initial coordination, ^b Coor. final = final coordination, ^c Dist. = interaction distance, ^d Char. = Mulliken net atomic charge. ^e 4f* = 4-fold on top of the surface, ^f Mg-O_{Tib} = Interaction distance in bidentate mode, ^g Mg-O_{Ti} = Interaction distance in monodentate mode, ^h O_s-Ti = Interaction distance in monodentate mode of Ti with O atoms in the surface, ⁱ O_s-Ti_b = Interaction distance in bidentate mode of Ti with O atoms in the surface.

rich in TiO₂ is required for quantifying the role and potential of photocatalysis on Mars. As example we have considered olivine as a substrate, since it has been discovered on meteorites, Mars and the Moon. The purpose of this work is to develop a model of a reactive layer of TiO₂ on an olivine substrate that can be used for space catalysis studies.

Olivine is an ultramafic rock, and a major component in the Earth's lithosphere and other planets, as Mars (Ody et al., 2013). It consists of magnesium, iron and silicates that form a complete solid solution between two end-members: *forsterite* (Mg-rich olivine) and *fayalite* (Fe-rich olivine). In space, forsterite has been found in meteorites and in the cometary dust of samples in the Stardust Mission (Lauretta et al., 2005). On Mars, olivine has been detected using remote and in-situ observations (Blake et al., 2013). Previous theoretical studies found that the (100) forsterite surface is one of the most reactive surfaces for water adsorption (Muralidharan et al., 2008; Stimpfl et al., 2006). The interaction of forsterite surfaces (Mg-rich olivine) with several molecules, such as water, glycine, ammonia, CO, CO₂, CH₄ etc. has been studied using several theoretical methodologies finding chemisorption processes in the solid-gas interphase (Asaduzzaman et al., 2014; Escamilla-Roa and Moreno, 2012, 2013; Escamilla-Roa et al., 2017).

In the present work we have analyzed the effect of three crystallographic phases of titanium oxide adsorbed onto (100) forsterite surface to simulate a regolith model. We have studied two surfaces of anatase, (001) and (100), and one surface (001) from Ti₂O₃ in order to generate thin layers, which are absorbed onto the non-dipolar forsterite surface. These surfaces can simulate different oxidation states of titanium oxide (Ti²⁺, Ti³⁺, and Ti⁴⁺). These different oxidation states can influence the distinct adsorption processes. This work specifically focuses on the role of the support on the structure of the active phases of TiO regolith. In particular, we investigate the electronic properties related with the adsorption process between the thin films of titanium oxide and the

olivine surface. The goal of this work is also to investigate at atomic level throughout DFT quantum mechanical calculations the effect of microscopic interactions of the forsterite surface with different thin films of Ti oxides.

2. Material and methods

In order to understand the adsorption energy and main geometrical structural parameters (bond distances) of different layers of TiO deposited on the non-dipolar forsterite (100) surface, we have used DFT calculations with the Dmol3 code within the Materials Studio package (Accelrys, 2009), considering periodical boundary conditions. The electronic calculations were made with the Generalized Gradient Approximation (GGA) with the PBE exchange correlation functional (Perdew et al., 1996) and a DNP basis set (double-zeta basis set augmented with polarization functions). The orbital cut-off quality was determined to be 0.1 eV atom⁻¹ energy accuracy threshold. We used Density functional semi-core Pseudopotentials (DSPP). The convergence criterion for the self-consistent field was 1×10^{-6} in the density matrix.

To determine the adsorption energy E^{ads} , we used the following equation:

$$E^{\text{ads}} = (E^{\text{x/forst-surf}} - E^{\text{forst-surf}} - nE^{\text{adsorbate}}) \quad (1)$$

where $E^{\text{x/forst-surf}}$, $E^{\text{forst-surf}}$, and $E^{\text{adsorbate}}$ are the energies of the complex of forsterite surface with the x-chemical species (TiO, Ti₂O₃ and TiO₂ adsorbed complexes) on the surface, the pristine forsterite surface, and the adsorbates involved, respectively. With respect to the electronic properties, this methodology has been previously used in theoretical models for exploring band gap in metals (Hernández-Haro et al., 2019).

Fig. 2. The direct adsorption onto non-dipolar (100) surface of forsterite of thin films that came from (100) and (001) anatase and Ti_2O_3 surfaces to simulate different regolith models of (a) TiO_2 , (b) Ti_2O_3 , and (c) TiO (view of the duplicate surface in all models).

2.1. Regolith models

Forsterite is an olivine mineral that could be considered as a component of Martian/Moon dust (Elphic et al., 2002; Lasue et al., 2018; Peters et al., 2008). The model of the mineral surface starts with an optimized crystal structure of forsterite, which consists of SiO_4 tetrahedral linked by divalent Mg cations with octahedral coordination. Previously we optimized the bulk and surface. The geometrical parameters, such as Mg–O and Si–O distances are in good agreement with previous results (de Leeuw et al., 2000; Watson et al., 1997). The building and optimization conditions of these structures were detailed in previous works (Escamilla-Roa and Moreno, 2012, 2013). The forsterite (100) surface was built up with periodical boundary conditions by cleaving the bulk structure of forsterite previously optimized. After this cleavage, a 1×2 unitcell of the (100) non-dipolar surface of forsterite was generated. An empty space of $20 \text{ \AA}$ on the (100) surface was created to explore the adsorption process. Then, the new lattice parameters of the surface are $u = 10.35$ and $v = 12.12 \text{ \AA}$. The surface's slab contains five SiO_4 horizontal planes with alternate Mg atoms. The reactivity between adsorbent and adsorbates has a strong relationship with the steps, terrace, and corners that are generated from the Mg atoms with low coordination in

surfaces (Escamilla-Roa and Sainz-Díaz, 2014; King et al., 2010). The cleavage of (100) surfaces produced the non-dipolar surface with several Mg atoms coordination. The Mg atoms of the relaxed slab of the top surface have different coordination: 4-fold (4f and 4f top) and 3-fold (3f) (Fig. 1a).

In the regolith models, each titanium oxide film came from (001) and (100) face cleavages of anatase and from the (100) face of Ti_2O_3 bulk structures. These surfaces were built up by cleaving a slice from the optimized bulk periodical structure of anatase/ Ti_2O_3 (Fig. 1b, c, d). With these cleavages the main oxidation states of Ti have been obtained: Ti^{2+} , Ti^{3+} , and Ti^{4+} . The first model consists of a thin film of TiO_2 that came from a cleavage in the (100) direction of an optimized anatase bulk structure. This film was increased in a 2×1 supersurface to cover the mineral forsterite surface. The layer is composed of eight Ti atoms with formal charge of +4 and sixteen O atoms (Fig. 1b). The second model of the layer represents Ti atoms with the formal charge Ti^{3+} that came from the cleavage in the (100) direction of the optimized Ti_2O_3 bulk structure, this film was increased in a 2×2 supersurface (Fig. 1c), being a Ti_8O_{12} layer. The third model corresponds to Ti oxide layer with Ti^{2+} formal charge, which is obtained of the cleavage in the (001) direction of the optimized anatase bulk structure and was increased in a 2×2 supersurface, being a Ti_4O_4 layer adsorbate (Fig. 1d). After the cleavage, all films were optimized alone at constant volume within a periodical box. In the adsorption process, the films of titanium oxide with their different oxidation states (Ti^{2+} , Ti^{3+} , and Ti^{4+}) were placed parallel onto the mineral surface at $4 \text{ \AA}$. The optimization procedure of these complexes was similar to that of the clean forsterite surface; i.e. at constant volume and in the slab, three upper SiO_4 planes were optimized and the rest of planes remained fixed. With the optimization process we can obtain the geometric parameters and adsorption energies of the adsorbed complexes. This methodology has been used successfully for describing similar adsorption processes (Escamilla-Roa and Moreno, 2012, 2013; Escamilla-Roa et al., 2013).

The coupling of both surfaces can be a good model of regolith. The Martian surface is exposed to an intense solar UV radiation and cosmic rays. The interaction with this highly ionizing environment may induce several processes such as photoionization, isomorphic substitution, generation of charged atoms and electrons (Perko et al., 2002) and reactive surfaces, such as that of forsterite proposed here. The presence of both materials on Mars conditions is an ideal scenario for producing regolith. The coupling of both minerals can have interesting implications in the photocatalytic activity. It has been postulated that photocatalytic processes may be relevant for atmospheric methane fluctuation, radicals and perchlorate productions (Bartoszek et al., 2011; Kim et al., 2013).

3. Results and discussion

3.1. Geometrical parameters of the regolith models

The optimization of the adsorbed complexes of different mono layers of titanium oxide over the mineral surface produced different regolith models. The adsorption energy is different for each model. In the regolith model with TiO_2 (Ti^{4+}), the adsorption of the layer onto the forsterite surface showed no significant change in the forsterite surface (Fig. 2a). In this regolith model the O atoms of the Ti oxide layer are bonded to the 4f and 3f Mg atoms of the surface. In some cases this adsorption changes the coordination of these Mg atoms with respect to the pristine surface. However, other Mg adsorption sites maintain the initial coordination, owing to the breaking of the pristine O–Mg bonds to join with the Ti atoms, these Mg atoms are indicated in Fig. 1a with the labels Mg_{25} and Mg_{68} . The $\text{Mg} \cdots \text{O}_{\text{Ti}}$ average interaction distance is $2.03 \text{ \AA}$. The Ti atoms are interacting with the surface O atoms forming two bond sites with bond distances $d(\text{Ti} \cdots \text{O}) = 1.94$ and $1.87 \text{ \AA}$ (Table 1). These values are similar to the bond distances of the anatase (001) surface ($d(\text{Ti} \cdots \text{O}) = 1.96$ – $2.04 \text{ \AA}$) (Escamilla-Roa et al., 2012). In this model the titanium dioxide is weakly adsorbed, the adsorption energy is -0.35 eV .

a)

b)

c)

d)

Fig. 3. Partial density of states (DOS) of (a) support (pristine surface of forsterite), (b) the TiO-fosterite, (c) Ti₂O₃-fosterite, and (d) TiO₂-fosterite complexes.

After the optimization of the Ti₂O₃ film onto forsterite, the adsorption energy is -9.78 eV being higher than in the above model. The geometrical parameters of this adsorbed complex changed due to strong interactions with the surface where many bond-breaking and bond-forming processes are produced. Some Mg atoms changed their coordination in the surface from 4f to 3f. In this place, the surface has been reconstructed on the atoms Mg₂₅, Mg₃₀, Mg₉₅ and Mg₁₀₀ (Fig. 1a). In this case two adsorption sites were found on the surface (Mg and O_s) to produce the following interactions: Mg...O_{Ti} and O_s...Ti. The Mg atoms have interaction distances of $d(\text{Mg}-\text{O}_{\text{Ti}}) = 2.13$ Å, in this site the Mg increases the coordination from 3f to 5f and the Ti₂O₃ O atom is coordinated to Mg atoms in a binuclear bidentate mode (Mg₄₈ and Mg₁₁₅). In Table 1, this interaction is indicated as Mg-O_{Tib}. Another interaction corresponds to Ti atoms that can be bonded to surface oxygens (O_s). We found several coordinations: monodentate (O_s-Ti) and bidentate binuclear (O_s-Ti_b) modes, whose average distance is 1.89 Å. The bidentate and monodentate coordinations of the Ti with the O atoms on the mineral produce rings on the top of the surface (Fig. 2b). Consequently, the interactions of thin Ti₂O₃ films with the mineral surface has an opposite behavior to the previous model (Ti⁴⁺) i.e. the adsorption energy is higher and the surface is modified due to the strong interactions with the forsterite surface.

The optimization of the regolith model where the TiO film is adsorbed on the forsterite surface shows that the thin layer forms rings with the mineral surface (Fig. 2c). In the same way of the above models, the optimized adsorbed complex shows significant geometrical changes in the interphase adsorbate-substrate, modifying strongly the bonds between TiO and forsterite. All atoms of the TiO film have been adsorbed

onto the surface. Four Mg atoms whose coordination was 4f in the pristine surface changed to 3f to produce the rearrangement of the surface (Fig. 1a) as in the Ti₂O₃ model (Table 1). On the other hand, O atoms of the TiO film were adsorbed on two Mg adsorption sites, the new bonds have an average distance of $\text{Mg}-\text{O}_{\text{Ti}} = 2.16$ Å. The Ti atoms in the film interact with surface's O atoms (O_s) in a bridging bidentate-binuclear mode whose average bond distance is $\text{Ti}-\text{O}_s = 1.96$ Å. The stability of TiO phase onto forsterite has enhanced due to bidentate-binuclear mode (O_s-Ti-O_s). In addition, the bidentate binuclear mode changed the coordination of the neighbor Mg atoms from 4f to 2f (Mg₆₈ and Mg₁₃₈). Similar behavior was observed in other previous adsorption studies on forsterite surfaces (Escamilla-Roa et al., 2017, 2018; Escamilla-Roa and Moreno, 2012; Escamilla-Roa and Sainz-Díaz, 2014). As a result of these strong alterations on the surface, the adsorption energy indicates an exothermic process (-29.08 eV). In this work this regolith model is the most reactive one, due to the TiO is strongly chemisorbed onto the mineral surface.

3.2. Electronic structure in the adsorption process

TiO is considered as a superconducting material (Wang et al., 2017). Then in this study we show that the electronic properties are related with the chemisorption or physisorption processes in the surface. Our results show that when the TiO is strongly adsorbed onto the forsterite surface with high adsorption energy, the band gap in the electronic density of state (DOS) is reduced near the Fermi level. In the anatase film (TiO₂) the behavior is the opposite because it is weakly adsorbed with lower

a)

b)

Fig. 4. Plots of the (a) adsorption energy, and (b) formal charge, as a function of the band gap energy in all optimized structures of regolith model.

adsorption energy.

The PDOS (Partial Density of States) profile of the pristine forsterite surface is depicted in Fig. 3a, indicating an energy gap of 2.914 eV. After the interaction process, the regolith with TiO showed significant changes with respect to the pristine surface. The band gap is close to 0.078 eV, which indicates a strong semiconducting behavior (Fig. 3b). The interaction of the Ti_2O_3 film with the forsterite surface reduces also the band gap to 0.20 eV but in a smaller degree than the TiO one (Fig. 3c). However, in the case of TiO_2 -regolith, the behavior was the opposite, the band gap is far from the Fermi level and the TiO_2 -film is weakly adsorbed. The band gap is the highest (2.029 eV) of the adsorption complexes studied (Fig. 3d). Therefore, a band gap similar to the support is found when a physisorption process is involved.

Comparing the PDOS of substrate (Fig. 3a) with those of the most reactive TiO and Ti_2O_3 film-forsterite complexes, one can observe the Ti-d orbitals appear at the Fermi level. Therefore, a strong interaction between the adsorbate and the mineral surface is suggested (Fig. 3b and c). This behavior has been earlier investigated in a theoretical study of the adsorption process on FeS (Dzade et al., 2014).

b)

Fig. 5. Plots of the reduction (Mulliken charges) process of (a) the Mg(25) atom on the surface, and (b) the oxidation of the surface O(8) atom after the adsorption process, as a function of the band gap energy in all optimized structures of regolith.

Fig. 6. Plots of the reduction process of Ti (Mulliken charges) after the adsorption process, as a function of the band gap energy in all optimized structures of regolith.

The relationship between the adsorption energy and the band gap energy above observed, invites to represent the band gap energy as a function of the adsorption energy in the regolith models studied [band gap energy = $f(\text{adsorption energy})$] that can be interpolated to a quadratic polynomial equation (Fig. 4a), showing an inverse relationship. The reactive regolith model with the highest adsorption energy is represented by the point in the lowest part of the graphic with the lowest band gap energy and the regolith model weakly adsorbed corresponds to the highest band gap energy (Fig. 4a). On the other hand; the band gap energy can be correlated with the Ti formal charge finding also a quadratic polynomial equation where the highest band gap corresponds to the highest formal charge of Ti (Fig. 4b).

3.3. Redox process

We have also explored the Mulliken net atomic charges in the interphase Ti_xO_y -film/forsterite. After the interaction, the exposed atoms in the substrate and adsorbate have modified their oxidation state. Experimentally, the chemical reduction of surface Ti atom in the adsorption processes is well known (Caballero et al., 1995; Choudhury et al., 1989; Malherbe et al., 1986). Recent experimental studies, using the ion bombardment for characterization of the deposition of Ti on surface, they have indicated that the most evident effect is the reduction of Ti in the region close to the surface (Pabón et al., 2015).

In the previous section 3.1 the rupture and formation of bonds in the adsorption process on the surface were discussed. Some Mg and O atoms in the surface were modified by the adsorption of Ti_xO_y -films (Table 1). The Mulliken atomic charges of the Mg, O and Ti atoms are related with the energy band gap. The charges of the main Mg atoms (Fig. 1b) in the interphase were plotted for TiO , Ti_2O_3 and TiO_2 -regoliths. Fig. 5a indicates that Mg(25) atom is more reduced when the regolith is chemisorbed (TiO) and the energy gap is the smallest. On the other hand, the Mulliken charge suggests that in the physisorbed TiO_2 -regolith, the Mg charge is similar to that in the pristine surface; which agrees with the low interaction TiO_2 /mineral surface. As it was expected, the surface O atoms related with the adsorption are as more oxidized as lower the band gap is (Fig. 5b) as a consequence the adsorption energy increases. Conversely, in the regolith weakly adsorbed the charge is weakly modified and is similar to O atoms in the substrate.

Finally, the analysis of Mulliken charges in the Ti atoms show a clear evidence of a Ti reduction process (Fig. 6). The Ti atoms of the chemisorbed regoliths undergo a strong reduction when they interact with the mineral surface. We consider that our results are in a good agreement with the experimental evidences that indicate that Ti is progressively reduced during the adsorption of Ti (Pabón et al., 2015). Our models suggest that the first deposition steps would be relating with a physisorption process in which the Ti atoms are not reduced and later these Ti atoms will be progressively reduced in the chemisorption process.

4. Conclusions

In this study we have detailed, from a theoretical point of view, the electronic properties and redox reaction that occurs in the adsorption process of different phases of titanium oxide (TiO , Ti_2O_3 , TiO_2) films onto forsterite (100) surface producing several regolith models. The models show different adsorption processes i.e. physisorption and chemisorption. Our results suggest that the TiO is the most reactive phase and its adsorption produces a strong exothermic effect and an atomic rearrangement in the mineral surface. The special stability of the TiO phase with respect to the rest of regoliths is due to the fact that Ti ions are coordinated with the surface O atoms in a bridging bidentate-binuclear mode. The electronic density of states (DOS) and atomic charges can describe the interaction processes that occur in the interphase mineral surface-adsorbates. The energy gap has a relationship with the adsorption energy and the redox processes. On the other hand, our results agree with the experimental results that predict that the Ti was reduced in the

most adsorbed complexes (TiO , Ti_2O_3). Moreover; the Mg atoms implicated in the chemisorption processes are also reduced, whereas the surface O atoms are oxidized. These calculations may be relevant for understanding future exploration missions of Mars and Moon, which can be directly related with the In-Situ-Resource-Utilization (ISRU) of regolith as potential photocatalytic surfaces. On the other hand, in materials science, this study can be a help for understanding the electronic properties to obtain new supports to photocatalytic processes. The studies reported here are the theoretical analyses required to complement the experiments that are currently under investigation by some of the authors of this group. In particular, we are presently working on the design of processes and prototypes for space operation (Moon Alchemist) that can induce certain reactions, such as methane production, through UV-photocatalytic processes supported by Martian or Moon regolith. These kind of theoretical calculations can help designing and understanding the properties of future catalytic materials for space. Furthermore, this may have applications also on Earth, as it can be used for environmental remediation and energy production.

Declaration of competing interest

Authors of the manuscript Ref: PSS_2018_301 entitled "DFT study of electronic and redox properties of TiO_2 supported on olivine for modeling regolith on Moon and Mars conditions" declare there are no conflicts of interest.

Acknowledgements

Authors acknowledges the Spanish MINECO projects CGL2014-55230-R, PCIN-2017-098, and FIS2016-77692-C2-2-P co-financed with European FEDER funds. We also would like to thank the generous support of Kempe and Wallenberg Foundations. MPZ, JMT, and EER recognize the ESA/Airbus/Air Liquide and Merck Space Exploration Masters challenge 2018 finalist award for Moon ISRU solutions for the Moon Alchemist proposal that uses Moon regolith with TiO_2 for methane production.

References

- Accelrys, 2009. Inc. Materials Studio, San Diego, U.S.A.
- Arvidson, R.E., et al., 2008. Spirit Mars rover mission to the Columbia Hills, Gusev crater: mission overview and selected results from the Cumberland ridge to home plate. *J. Geophys. Res.: Planets* 113, E12S33.
- Asaduzzaman, A.M., et al., 2014. A computational investigation of adsorption of organics on mineral surfaces: implications for organics delivery in the early solar system. *Earth Planet. Sci. Lett.* 408, 355–361.
- Barnard, A.S., Zapol, P., 2004. Effects of particle morphology and surface hydrogenation on the phase stability of TiO_2 . *Phys. Rev. B* 70 (23), 235403.
- Barnard, A.S., Zapol, P., Curtiss, L.A., 2005. Modeling the morphology and phase stability of TiO_2 nanocrystals in water. *J. Chem. Theory Comput.* 1 (1), 107–116.
- Bartoszek, M., Weeks, M., Jakobs, G., Möhlmann, D., 2011. Photochemically induced formation of Mars relevant oxygenates and methane from carbon dioxide and water. *Planet. Space Sci.* 59 (2), 259–263.
- Blake, D.F., et al., 2013. Curiosity at gale crater, Mars: characterization and analysis of the rocknest sand shadow. *Science* 341 (6153), 1239505.
- Bradford, M.C.J., Vannice, M.A., 1999. CO_2 reforming of CH_4 . *Catal. Rev.* 41 (1), 1–42.
- Bridges, J.C., et al., 2015. Diagenesis and clay mineral formation at gale crater, Mars. *J. Geophys. Res.: Planets* 120 (1), 1–19.
- Caballero, A., Espinós, J.P., Fernández, A., Leinen, D., González-Elipe, A.R., 1995. Surface modification of oxide materials subjected to low energy ion bombardment: a XAS study. *Nucl. Instrum. Methods Phys. Res. Sect. B Beam Interact. Mater. Atoms* 97 (1), 397–401.
- Choudhury, T., Saied, S.O., Sullivan, J.L., Abbot, A.M., 1989. Reduction of oxides of iron, cobalt, titanium and niobium by low-energy ion bombardment. *J. Phys. D Appl. Phys.* 22 (8), 1185–1195.
- Civis, S., et al., 2017. The origin of methane and biomolecules from a CO_2 cycle on terrestrial planets. *Nature Astron* 1 (10), 721–726.
- de Leeuw, N.H., Parker, S.C., Catlow, C.R.A., Price, G.D., 2000. Modelling the effect of water on the surface structure and stability of forsterite. *Phys. Chem. Miner.* 27, 332–341.
- Diebold, U., 2003. The surface science of titanium dioxide. *Surf. Sci. Rep.* 48 (5), 53–229.
- Do, J.Y., Kwak, B.S., Park, S.-M., Kang, M., 2016. Effective carbon dioxide photoreduction over metals (Fe-, Co-, Ni-, and Cu-) incorporated TiO_2 /basalt fiber films. *Int. J. Photoenergy* 1–12, 2016.

- Dzade, N.Y., Roldan, A., de Leeuw, N.H., 2014. The surface chemistry of NO_x on mackinawite (FeS) surfaces: a DFT-D2 study. *Phys. Chem. Chem. Phys.* 16 (29), 15444–15456.
- Edwards, P.H., et al., 2017. Basalt–trachybasalt samples in gale crater. *Mars* 52 (11), 2931–2410.
- Elphic, R.C., et al., 2002. Lunar Prospector neutron spectrometer constraints on TiO₂. *J. Geophys. Res.: Planets* 107 (E4), 8-1-8-9.
- Escamilla-Roa, E., Martin-Torres, J., Sainz-Díaz, C.I., 2018. Adsorption of methane and CO₂ onto olivine surfaces in Martian dust conditions. *Planet. Space Sci.* 153, 163–171.
- Escamilla-Roa, E., Moreno, F., 2012. Adsorption of glycine by cometary dust: astrobiological implications. *Planet. Space Sci.* 70 (1), 1–9.
- Escamilla-Roa, E., Moreno, F., 2013. Adsorption of glycine on cometary dust grains: II—effect of amorphous water ice. *Planet. Space Sci.* 75 (1), 1–10.
- Escamilla-Roa, E., Moreno, F., López-Moreno, J.J., Sainz-Díaz, C.I., 2017. Atomistic and infrared study of CO-water amorphous ice onto olivine dust grain. *Planet. Space Sci.* 135, 17–26.
- Escamilla-Roa, E., Sainz-Díaz, C.I., 2014. Amorphous ammonia–water ice deposited onto silicate grain: effect on growth of mantles ice on interstellar and interplanetary dust. *J. Phys. Chem. C* 118 (7), 3554–3563.
- Escamilla-Roa, E., Sainz-Díaz, C.I., Huertas, F.J., Hernández-Laguna, A., 2013. Adsorption of molecules onto (1014) dolomite surface: an application of computational studies for microcalorimetry. *J. Phys. Chem. C* 117 (34), 17583–17590.
- Escamilla-Roa, E., Timón, V., Hernández-Laguna, A., 2012. DFT study of the adsorption of Ni on Anatase (001) surface. *Comput. Theor. Chem.* 981, 59–67.
- Gounelle, M., et al., 2005. Small Antarctic micrometeorites: a mineralogical and in situ oxygen isotope study. *Meteorit. Planet. Sci.* 40, 917–932.
- Grant, F.A., 1959. Properties of rutile (titanium dioxide). *Rev. Mod. Phys.* 31 (3), 646–674.
- Greeley, R., et al., 2004. Wind-related processes detected by the Spirit rover at Gusev crater, Mars. *Science* 305 (5685), 810–813.
- Herkenhoff, K.E., et al., 2004. Textures of the soils and rocks at Gusev crater from spirit's microscopic imager. *Science* 305 (5685), 824–826.
- Hernández-Haro, N., Ortega-Castro, J., Martynov, Y.B., Nazmitdinov, R.G., Frontera, A., 2019. DFT prediction of band gap in organic-inorganic metal halide perovskites: an exchange-correlation functional benchmark study. *Chem. Phys.* 516, 225–231.
- Hurowitz, J.A., et al., 2017. Redox stratification of an ancient lake in Gale crater, Mars. *Science* 356 (6341), eaah6849.
- Kim, G.J., Cho, D.-S., Kim, K.-H., Kim, J.-H., 1994. The reaction of CO₂ with CH₄ to synthesize H₂ and CO over nickel-loaded Y-zeolites. *Catal. Lett.* 28 (1), 41–52.
- Kim, Y.S., Wo, K.P., Maity, S., Atreya, S.K., Kaiser, R.L., 2013. Radiation-induced formation of chlorine oxides and their potential role in the origin of martian perchlorates. *J. Am. Chem. Soc.* 135 (13), 4910–4913.
- King, H.E., et al., 2010. Computer simulations of water interactions with low-coordinated forsterite surface sites: implications for the origin of water in the inner solar system. *Earth Planet. Sci. Lett.* 300 (1–2), 11–18.
- Lasue, J., et al., 2018. Martian eolian dust probed by ChemCam. *Geophys. Res. Lett.* 45, 10968–10977.
- Lauretta, D., Keller, L.P., Messenger, S., 2005. Supernova olivine from cometary dust. *Science* 309, 737–741.
- Linsebigler, A.L., Lu, G., Yates, J.T., 1995. Photocatalysis on TiO₂ surfaces: principles, mechanisms, and selected results. *Chem. Rev.* 95 (3), 735–758.
- Malherbe, J.B., Hofmann, S., Sanz, J.M., 1986. Preferential sputtering of oxides: a comparison of model predictions with experimental data. *Appl. Surf. Sci.* 27 (3), 355–365.
- Moore, H.J., et al., 1999. Soil-like deposits observed by Sojourner, the Pathfinder rover. *J. Geophys. Res.: Planets* 104 (E4), 8729–8746.
- Muralidharan, K., Deymier, P., Stimpfl, M., de Leeuw, N.H., Drake, M.J., 2008. Origin of water in the inner Solar System: a kinetic Monte Carlo study of water adsorption on forsterite. *Icarus* 198 (2), 400–407.
- Noguchi, T., et al., 2011. A chondrule-like object captured by space-exposed aerogel on the international space station. *Earth Planet. Sci. Lett.* 309, 198–206.
- Ody, A., et al., 2013. Global investigation of olivine on Mars: insights into crust and mantle compositions. *J. Geophys. Res.: Planets* 118 (2), 234–262.
- Pabón, B.M., et al., 2015. Formation of titanium monoxide (001) single-crystalline thin film induced by ion bombardment of titanium dioxide (110). *Nat. Commun.* 6, 6147.
- Perdew, J.P., Burke, K., Ernzerhof, M., 1996. Generalized gradient approximation made simple. *Phys. Rev. Lett.* 77, 3865.
- Perko, H.A., Nelson, J.D., Green, J.R., 2002. Review of martian dust composition, transport, deposition, adhesion, and removal. *Space 2002 and Robotics*, pp. 176–189.
- Peters, G.H., et al., 2008. Mojave Mars simulant—characterization of a new geologic Mars analog. *Icarus* 197 (2), 470–479.
- Rajh, T., et al., 2004. Charge transfer across the nanocrystalline-DNA Interface: probing DNA recognition. *Nano Lett.* 4 (6), 1017–1023.
- Schrauzer, G.N., Guth, T.D., 1977. Photocatalytic reactions. 1. Photolysis of water and photoreduction of nitrogen on titanium dioxide. *J. Am. Chem. Soc.* 99 (22), 7189–7193.
- Stimpfl, M., Walker, A.M., Drake, M.J., de Leeuw, N.H., Deymier, P., 2006. An angström-sized window on the origin of water in the inner solar: atomistic simulation of adsorption of water on olivine. *J. Cryst. Growth* 294, 83–95.
- Wang, D., et al., 2017. Enhanced superconductivity in rock-salt TiO. *ACS Omega* 2 (3), 1036–1039.
- Wang, S., Lu, G.Q., Millar, G.J., 1996. Carbon dioxide reforming of methane to produce synthesis gas over metal-supported Catalysts: state of the art. *Energy Fuels* 10 (4), 896–904.
- Watson, G.W., Oliver, P.M., Parker, S.C., 1997. Computer simulation of the structure and stability. *Phys. Chem. Miner.* 25, 70–78.
- Webster, C.R., et al., 2015. Mars methane detection and variability at Gale crater. *Science* 347, 415–417.
- Webster, C.R., et al., 2018. Background levels of methane in Mars' atmosphere show strong seasonal variations. *Science* 360, 1093–1096.
- Witze, A., 2019. Mars rover detects 'excitingly huge' methane spike. *Nature*. <https://doi.org/10.1038/d41586-019-01981-2>.
- Yan, W., et al., 2004. Surface Sol–Gel modification of mesoporous silica materials with TiO₂ for the assembly of ultrasmall gold nanoparticles. *J. Phys. Chem. B* 108 (9), 2793–2796.
- Zhang, Z., Verykios, X.E., 1996. Carbon dioxide reforming of methane to synthesis gas over Ni/La₂O₃ catalysts. *Appl. Catal. Gen.* 138 (1), 109–133.