Adsorption of Fe_3O_4 nano clústers on montmorillonite

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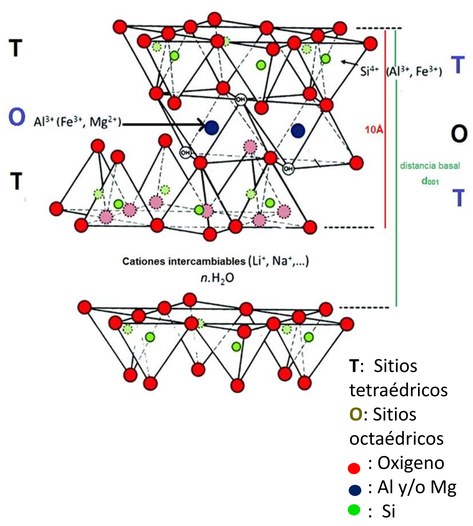
Introduction

- Industrialization has a great impact on environmental health, potentially contributing to an increament in pollution, which is critical for water reservoirs since it affects the whole life on the planet.
- Many of the methods used for remediation technologies are based on the sorption process. Clay minerals such as montmorillonite (MMT) are among the materials used [1].
- The sorption capacity of heavy metals in MMT has been verified both on the surface and in the interlaminar space.
- Providing magnetic properties to materials suitable for remediation would allow their manipulation using external magnetic fields for recovery, thus reducing potential health risks in the process [2].
- The aim of this work is to model of the adsorption of magnetic nano-particles (MNP) on different MMT surfaces and sites

Study system



Montmorillonite (MMT)

It is a 2:1 type phyllosilicate formed by two tetrahedral layers and one octahedral layer that constitute a TOT sandwich structure.

T (tetrahedra): constitute of 4 oxygen atoms surrounding a central atom Si^{4+}.

O (octahedra): made up of 6 oxygen or OH atoms surrounding a cation Al^{3+} o Mg^{2+}.

The oxygens that constitute these structures are classified as basal, apical or belonging to OH. The apical ones are those that link the T and the O, while the basal ones are the rest of the T.

Chemical formula of Na-MMT

$(Na_{0.41}[(MgAl_3O_8(OH)_4(Si_8O_{12})]_2.\ 4(H_2O)$ (Na-MMT)

In natural samples, iron impurities occur that isomorphically replace Al^{3+} o Mg^{2+} in the octahedral sites.

This work present preliminary results of magnetite (Fe_3O_4) nano-clusters adsorption modeling on different surfaces of Na-MMT, through ab initio calculations

Details

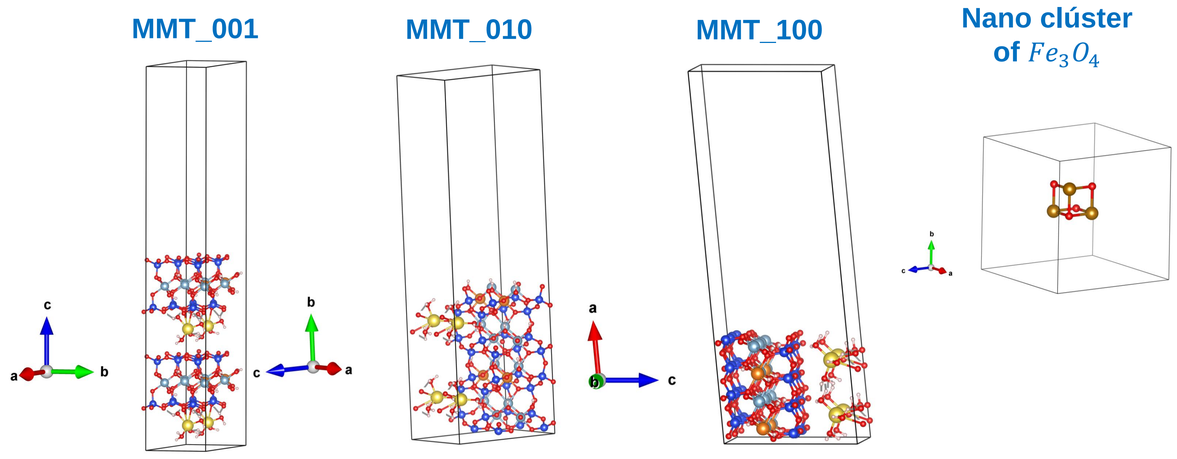
Model Details

- **Ab-initio calculations** within the Density Functional Theory, using the pseudopotentials method and plane waves as implemented in the **Quantum Espresso code.**
- Correlation-exchange term: GGA-PBE.
- Norm-conserving pseudopotentials.
- The modeling of the surfaces was carried out from the pristine structure of Na-MMT.
- The Fe_3O_4 nano-cluster structure was extracted as part of experimental the magnetite structure.
- For the study of adsorption, steps were taken to approach the cluster to the surface under investigation.
- To analyze the sorption processes at each step, structural relaxation of the relevant atoms where performance and the total energy was calculated.

Starting from the unit cell, different supercells were built: 2x1x2, 2x2x1 and 2x2x1 thus forming orientations 001, 010 and 100 (MMT_001, MMT_010 and MMT_100 respectively). For the surface simulation a 25 Å thick vacuum slab was inserted.

In turn, for the optimization of the Fe_3O_4 cluster, it was placed at the center of a cubic cell with lattice parameter of 10Å.

MMT_001 **MMT_010** **MMT_100** **Nano clúster of Fe_3O_4**



Through total energy analysis, the most probable surface and adsorption sites were established.

Results

Preliminary results

- The total energy for each of the surfaces were calculated to obtain the formation energy.
- The results show in figure 1.
- It can be see that **MMT_001** has the lower formation energy.

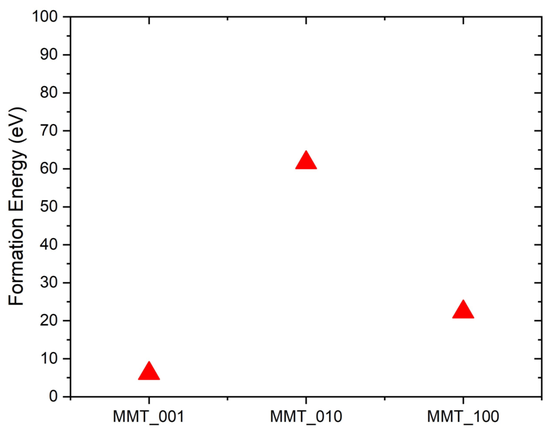


Figure 1: Total energy of MMT_001, MMT_010 and MMT_100.

- The MMT_001 surface is composed by ring siloxanes. Different adsorption sites were analyzed: a Si cation, an O anion and a the ring central hole which has a OH in the lower layer, (see figure 2b), For each place we calculated the adsorption energy by:

$$E_{ads} = E_{MMT_{001}+Fe_3O_4} - [E_{Fe_3O_4} + E_{MMT\_001}]$$

Where:

$E_{MMT_{001}+Fe_3O_4}$ is the energy of the surface with the Fe_3O_4 clúster,

$E_{Fe_3O_4}$ is the energy of the Fe_3O_4 cluster at the center of a cubic cell.

E_{MMT_001} is the surface energy

- The nanocluster approachs the surface by steps, starting from a distance of 8Å, and then approaching every 2Å until reaching the selected sites [3].

View video relaxation

The result of adsorption energy can be seen in Figure 3

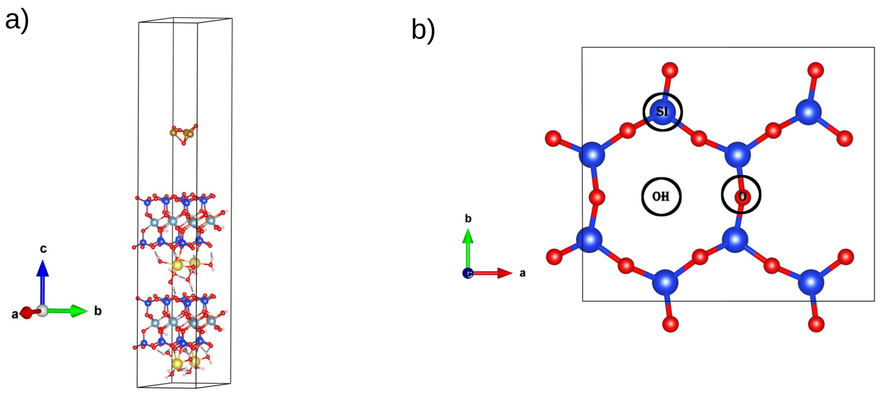


Figure 2: a) side view of MMT_001 with the Fe_3O_4 nanocluster, b) top view of the siloxane rings and the explored adsorption sites indicated with black circles.

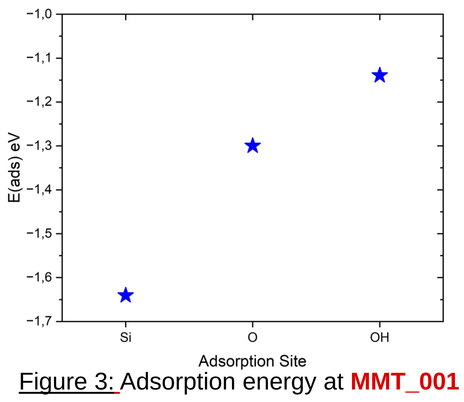


Figure 3: Adsorption energy at **MMT_001** sites

From the data shown in Figure 3, it can be inferred that the most likely adsorption site is **site of Si** with an adsorption energy of **-1.64 eV**.

Conclusions

Conclusions

- It was determined that the most probable surface for the formation of MMT is **MMT_001.**
- This work shows that the cluster Fe_3O_4 is adsorbed by the **MMT_001** surface.
- It was possible to determine that the most stable adsorption site is **Site of Si** with am adsorption energy of -1.64 eV.

References

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