Adsorption of NO on Al_2O_3 surfaces from DFT and Thermodynamics

April 23, 2022

This is semi-individual and semi-group assignment. The individual part involves calculation of adsorption energy for different structures. The team part is about collecting individual data from all students to plot a phase diagram of the surface.

1 Problem statement

Compute the adsorption of NO at different coverage on $p(1 \times 1)$ γ-$Al_2O_3(100)$ surface using density functional theory (GGA-PBE) and atomistic thermodynamics.

2 Objectives and goal

FHI-aims and Abinit have a fundamental difference between each other: FHI-aims is full-electron code with atomic orbitals basis sets, while Abinit uses plane-wave basis set and pseudopotentials to describe core electrons. Plane waves are delocalized over entire space, that is why they are good for describing infinite crystals, while atomic basis set is localised, which is good for description of the finite or semi-finite objects: surfaces, clusters, nanowires. The ultimate goal of this lab work is to calculate surface phase diagrams of γ-alumina surfaces in the presence of NO atmosphere, which is practically important for catalytic conversion of NO.

Students shall:

1) learn how to use a code with atomic-orbitals basis sets.

2) learn how to use atomic simulation environment (ASE) package to manipulate atomic structures, in particular construct surfaces from bulk unit cell.

3) go through the process of writing a paper by a team of scientists who obtain results and compile them to obtain a group result.

3 Step-by-step guide

In this lab we are using *light* basis settings for all atomic species.

Optimized bulk structure of γ-Al_2O_3 can be found in `/tmp/Lab2/`

Individual part:

0) relax NO molecule with FHI-aims to define the bond length. Write the bondlength to the report. (**1 point**).

1) Install atomic simulation environment (ASE):

```
https://wiki.fysik.dtu.dk/ase/install.html
```

2) Cut the slab out of crystal structure. Use one layer and 50 A vacuum sharp. Share the picture of your slab in two views (top view and side view) in the report. **(1 point)**

You will need functions `read_aims` from the module `ase.io.aims` in order to read bulk structure from file. To cut the slab, you have to apply function from `ase.build` module

```
surface(bulk, ([h,k,l]), layers=N, vacuum=W, tol=T).
```

Here `bulk` is bulk structure that you have read from the file, `[h,k,l]` are Miller indices of the surface you want to cut, `N` is number of layers, `W` is the width of the vacuum that you add to the structure, `T` is the tolerance that you use. `T` should be at least 10^{-5} .

Full description of `surface()` function can be found here:

```
https://wiki.fysik.dtu.dk/ase/ase/build/surface.html
```

Function `write_aims` can be used to write `geometry.in` file for resulting slab.

3) Relax slab with FHI-aims. Use $4 \times 4 \times 1$ k-point grid and 'light' basis set. Write the energy of the relaxed slab in your report. **(1 point)**

Group part:

4) Define and distribute structures with adsorbed NO molecules among students, so that each student calculates at least 3 structures with distinct coverages. You need to try 3 different coverages (1-6 NO molecules, not necessarily all of them, some coverages can be tested with different placements, it is up to you). Make sure that you do not take structure which is already taken. The coverages that you are supposed to try are specified in google docs.

WARNING! If two students have the same structure, both of them will get 0 points for it. Cooperate and make sure everyone uses different structures!

In order to help you to meet requirements of the lab, there is a spreadsheet, where each student should submit `geometry.in` file for his or her structures by April 29 23:59 (**1 point**). If you fail to submit on time or submit 'prohibited' structures mentioned above, you will not be able to get that point. Clickable link for the spreadsheet is in Telegram chat.

Individual part:

5) (**1 point per each relaxation, 3 points overall**) Relax one of your structures (preferably with the smallest coverage) with adsorbed NO. Try different options for relaxation:

a) relax the whole structure. Write the energy that you have obtained.

b) fix 3 bottom atomic layers, relaxing only the top layer. Write the energy that you have obtained.

c) fix 2 bottom atomic layers, relaxing only 2 top layers. Write the energy that you have obtained.

Specify `use_dipole_correction` keyword for your slab calculation.

Compare differences in adsorption energies (**1 point**) for slabs with different relaxed number of layers obtained by you and other students, choose the optimal number of fixed layers (as many as possible, but the differences in adsorption energy should be < 0.05 eV) based on all data.

6) Relax other two structures with higher coverages with 2 bottom layers fixed. (**1 point per each relaxation, 2 points overall**) Write the energy that you have obtained for each structure.

It is convenient to visualise slab and add NO molecules using visualisation and editing function is ASE:

```
from ase.visualize import view
view(atoms)
```

or simply `atoms.edit()`, where `atoms` is the structure that you want to edit. Use `add atoms` option while you are in editing regime.

7) Adsorption energy per molecule is the difference between the structure with adsorbed molecules minus energy of slab and the molecules separately, divided by total number of adsorbed molecules:

$$E_{\text{ads}} = \frac{E_{\text{slab}+m\text{NO}} - (E_{\text{slab}} + mE_{\text{NO}})}{m} \tag{1}$$

where m is number of adsorbed NO molecules per supercell on the surface.

Surface Gibbs free energy per surface area:

$$\gamma = \frac{1}{A}\left(E_{\text{slab}+m\text{NO}} - (E_{\text{slab}} + mE_{\text{NO}}) - m\Delta\mu_{\text{NO}}(T, p_{\text{NO}})\right) \tag{2}$$

where A is the area of the surface supercell, and

$$\Delta\mu_{\text{NO}}(T, p_{\text{NO}}) = \Delta\mu_{\text{NO}}(T, p^{\circ}_{\text{NO}}) + kT\ln\left(\frac{p_{\text{NO}}}{p^{\circ}_{\text{NO}}}\right) \tag{3}$$

p°_{NO} is a standard pressure, and $\Delta\mu_{\text{NO}}(T, p^{\circ}_{\text{NO}})$ at different T can be found in thermochemical reference tables (`https://janaf.nist.gov`).

Group part:

8) Share the results of the **total energies for your structures with adsorbed molecules** of NO (NOT adsorption energies). The deadline is May 12th 23:59.

Individual part:

9) Plot a (T,p_{NO}) phase diagram using the low-energy structures identified in the previous step. More detailed information about phase diagrams see in 'Atomistic Thermodynamics' Lecture. **5 points**

4 Structure of report

Each student provides his or her own report. Each task that gives points from step-by-step guide should be reflected in your report either by figures, or by tables or by text description.

1) Introduction section and problem statement (1-2 paragraph, not more than 1/2 a page). Describe the problem that you are solving. Do a brief search and explain why NO adsorption @ Γ-alumina is an important problem to consider. You can start your search with this paper (1) and go to its references if necessary.

2) Computational details section for all steps of your calculations (basis set choice, k-points choice, geometry)

a) NO relaxation with description of all details

b) Description of creating surface and relaxing slab

c) Testing

d) Description of NO adsorption calculation

3) Results and discussion.

Speculate on results of your calculations: how did geometry change, what are adsorption energies and Gibbs free energies. Append side and top views of (a) slab itself, (b) slab with adsorbed NO molecules. Describe how you obtained phase diagram and speculate on it.

4) Conclusion. Make the brief summary of your work in 1-2 paragraphs.

References

[1] Z. Liu, L. Ma, and A. S. Junaid, "No and no2 adsorption on al2o3 and ga modified al2o3 surfaces: a density functional theory study," *The Journal of Physical Chemistry C*, vol. 114, no. 10, pp. 4445–4450, 2010.