

Assignment A4 - Kinetic Modeling

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Gold, platinum, and rhodium are all widely used metals for catalytic reactions. In this task, you will, from scratch, model the kinetics of the CO oxidation over these three metals (catalysts). The first tasks will be dedicated to determine the correct structures of the models, and calculate important energies. For the DFT calculations, I recommend using plane waves with the 'PBE' exchange-correlation functional. Suitable cutoff energy and number of k-points for the bulks are 450 eV and (12, 12, 12), respectively. The code below shows how this is done.

```
from gpaw import GPAW, PW

calc = GPAW(xc = 'PBE',
            mode=PW(450),
            kpts=(12, 12, 12),
            txt='calculation.txt')
```

In the second part, you will use the energies you have calculated and model the kinetics of the reaction over the three different catalysts. This way of modeling shows how we can predict which catalyst is most suitable for a specific reaction, and we do not have to spend a lot of time, and money, to test them all. But first, a little bit of theory about kinetic modeling! The rate of the CO oxidation reaction can, with a few tricks, be solved analytically. In the model, we are not interested in the detailed behavior of what happens on the surface, but rather the "average behavior"; more precisely, the fractional coverages on the surface. For example, if 20% of the metal surface is covered by CO at time t , then the coverage of CO is $\theta_{\text{CO}}(t) = 0.2$. We do *not* account for the attraction/repulsion between species on the surface, and therefore, you must also be careful not to incorporate any in your energy calculations. The time derivative of the coverage of i w.r.t. time is expressed as

$$\frac{d\theta_i}{dt} = \sum_j r_j(\boldsymbol{\theta}) n_{i,j}, \quad (1)$$

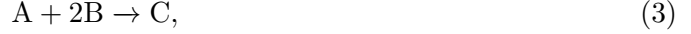
where r_j is the rate of reaction j , and $n_{i,j}$ is the stoichiometric coefficient for species i in reaction j . Note that the reaction rate is a function of the coverages.

The reaction rates are sometimes very hard to determine. Generally, they can be expressed as

$$r = f(\boldsymbol{\theta}) \underbrace{\nu e^{-E_a/k_B T}}_{k \text{ (rate constant)}}. \quad (2)$$

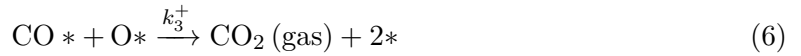
E_a is the activation energy of the reaction. ν is a complicated term, and will in this task be approximated to $\nu = 1 \cdot 10^{12} / \text{s}$. The function $f(\boldsymbol{\theta})$ is in this case much easier. It is simply the probability that the reacting species on the surface are present at the point of reaction.

Consider the reaction:



then, it is the probability of, at the point of reaction, having one A and two B. So $f(\boldsymbol{\theta}) = \theta_A \theta_B^2$. For an adsorption on the surface, you would need empty sites, therefore, the rate is dependent on $\theta_{\text{empty-sites}}$.

The different elementary reactions in the CO oxidation reaction are



where a lonely $*$ denotes an empty site and a $*$ together with an O atom/CO molecule indicates that it is bound to the surface. It is assumed that the oxygen molecules dissociate on the surface directly on impact.

For adsorption processes, the reaction rate is expressed as

$$r = f(\boldsymbol{\theta}) p k^+ = f(\boldsymbol{\theta}) \frac{pA}{\sqrt{2\pi m k_B T}}, \quad (7)$$

where p is the partial pressure, A is the area of the site, m is the mass of the molecule, k_B is Boltzmann's constant, and T is the temperature.

For adsorption/desorption events one often assumes equilibrium conditions (that Eq. 1 is equal to zero). The equilibrium constants, K then gives us the ratio between the adsorption rate and the desorption rate constants, as

$$K = \frac{k_{\text{ads}}}{k_{\text{des}}} = e^{-S_{\text{gas}}/k_B} e^{(E_{\text{gas}} - E_{\text{adsorbed}})/k_B T}, \quad (8)$$

where S_{gas} is the entropy of the molecule in the gas phase. We here assume that the adsorbed species have zero entropy.

The entropy of the molecule in gas phase can be beautifully calculated by combining DFT and your knowledge of thermodynamics, i.e., we will obtain it via the partition function! The partition function is a product between the translational, rotational and vibrational partition functions.

$$Q = Q_{\text{trans}} Q_{\text{rot}} Q_{\text{vib}}. \quad (9)$$

For a diatomic molecule these are given by

$$Q_{\text{trans}} = V \left(\frac{2\pi m k_{\text{B}} T}{h^2} \right)^{3/2} \quad (10)$$

$$Q_{\text{rot}} = \frac{8\pi^2 I k_{\text{B}} T}{\sigma h^2} \quad (11)$$

$$Q_{\text{vib}} = \frac{1}{1 - \exp\{-\varepsilon/k_{\text{B}}T\}}. \quad (12)$$

Here, m is the mass of the molecule, I is the moment of inertia, σ is the symmetry number (2 if the molecule has an inversion center and 1 otherwise), ε is the energy of the vibrational mode, k_{B} is the Boltzmann constant, h is Planck's constant, and T is the temperature. (The neglect of zero-point energy might annoy some of you. But they are roughly the same in the gas phase and on the surface, so in the end, they cancel out.) The entropy is now obtained from the partition function as

$$S = \frac{\partial}{\partial T} (k_{\text{B}} T \ln Q). \quad (13)$$

You do not have to write a complete report, but make sure to describe your thought process, motivate your answers and show all calculations and codes that you have used. It is always nice to see figures of your structures. (Which might also aid me in helping you with potential errors, so win-win.)

Good luck!

Task 1 : Determination of lattice parameters (1p)

Construct bulk gold, platinum, and rhodium and compute the lattice parameters. The correct lattice parameter is the one that minimizes the energy of the bulk metal. What lattice parameters did you get for the three different metals? How does it compare with experimental values?

Hint: The energy follows the same behavior as a harmonic oscillator, i.e., a few different, well-guessed lattice parameters and corresponding energies should be enough to find the optimal lattice parameter.

Task 2 : Cohesive Energies (1p)

It is important to know that the energies calculated with DFT are not cohesive energies. We do not have a reference yet. In this task, you should determine the cohesive energy of the bulk metals. Use the minimum energies obtained from Task 1. The DFT energies of a gold atom, platinum atom and rhodium atom are -0.158 eV, -0.704 eV and -1.218 eV, respectively.

Task 3 : Construct the surfaces (1p)

The CO-oxidation happens on the surface of the metals. Therefore, you also need to construct the surfaces. Use the lattice parameters obtained in Task 1 to construct the (111)-surfaces of the three metals. (This facet is the lowest in energy and, therefore, highly dominant in occurrence.) Construct a 3-layered 3×3 surface cell, with 6 \AA of vacuum in both the positive and negative z-direction. Periodicity in the x -and y-direction will give you infinite surfaces with 12 \AA distance between the periodic slabs in the z-direction. Keep the same cutoff energy as in the previous task. Here, you have a considerably larger cell than in previous tasks. Therefore your k-point sampling in the reciprocal space does not need to be as great as in previous tasks; use (4, 4, 1) instead. Relax the surfaces and determine the energies. What are the surface energies of the three metals? If we had an alloy consisting of all three metals, which metal would be dominant on the surface (in vacuum conditions)?

Hint: The surface energy is not the same as the energy of the surface. See: https://en.wikipedia.org/wiki/Surface_energy

Task 4 : Reference O_2 and CO (1p)

You now know the energy of the surface. In order to calculate the adsorption energy of a molecule on a surface, we also need to know the energy of that molecule in the gas phase. Calculate the energy of the O_2 molecule and the CO molecule. Your k-point sampling should consist only of the gamma-point.

Hint: Make a box with length $\approx 12 \text{ \AA}$ and insert the molecule.

Hint 2: Are the molecules spin-polarized?

Task 5 : Entropy (2p)

Perform a vibrational analysis of the gas phase molecules. What is the entropy of O₂ and CO at 300 K and 1 bar? Does it agree with experimental results?

Task 6 : Adsorption of O and CO (4p)

Calculate the adsorption energies for an O atom and a CO molecule adsorbing on the surfaces. Relax until the forces acting on each atom are all below 0.1 eV/Å. Try to find the most stable adsorption site and orientation in the literature.

Hint: The distance between the adsorbed species and a metal atom is around 2 Å in all cases.

With the use of scaling relations, you can now determine the activation energy, E_a , for the reaction between CO and O. This energy is determined from

$$E_a = -0.3 (E_{\text{ads}}(\text{O}) + E_{\text{ads}}(\text{CO})) + 0.22 \text{ eV}. \quad (14)$$

Show the structure of your adsorbed species on the surface. What are the two adsorption energies and the activation energy for the formation of CO₂ on the three different metal catalysts?

Task 7 : The Kinetic Analysis (14p)

Find analytical expressions for the fractional coverage of CO and O at *equilibrium conditions* in terms of the equilibrium constants. You may assume that the rate of CO₂ formation is significantly lower than the adsorption/desorption rates. Determine the formation rate of CO₂ at 1 atm CO pressure and 1 atm O₂ pressure in the temperature range 100-2000 K over the three different metals. The entropy of the adsorbed species on the surface are all zero. Show plots for the coverages and CO₂ formation rate in the entire temperature interval.

What does the formation rate mean in this case? You have a value, but how can we use that value to determine the formation rate of CO₂ on a surface with a given area? Which catalyst is the best? Does it agree with experiments?

Task 8 : Thoughts (6p)

You should observe one distinct peak of the formation rate of CO₂, for each catalyst. Why is this peak located at different temperatures for the various catalysts? Which factors affect the height and location of the peak?

Can you name at least three limitations with the methods you have used to determine the reaction rate? (Uncertainties from DFT are not one of them; in our world, DFT is the golden standard.)

Suppose you were to take attraction/repulsion between adsorbed species into account. How would that change the coverage on the surface and the reaction rate?

How would you design your dream catalyst for this reaction? Is a mono-metallic (111)-surface the best choice? Motivate your answers.