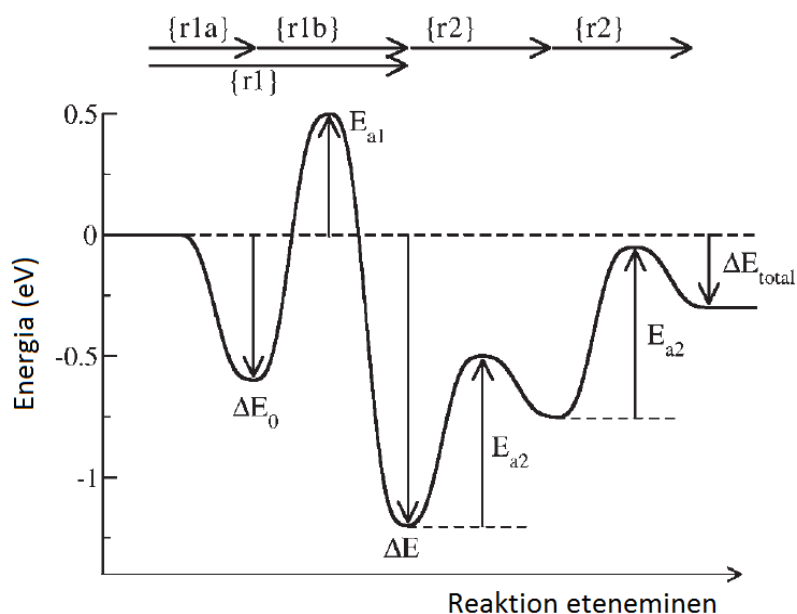


Computational study of surface catalysis

The catalyst study is one of the key topics of surface calculations. One need to keep in mind that there are several steps in the catalytic reactions. Typically these are

- 1) molecular adsorption and co-adsorption
- 2) surface diffusion
- 3) surface reaction steps
- 4) production dissociation

Some reaction barrier is associated to (almost) all these reaction steps. Luckily only the largest barriers is the rate limiting step only that need to be know accurately. But we seldom know which is the largest barrier and often barrier heights might depend on the adsorbent concentrations. The surface may have steps that are more active than the flat surface. In general the reaction studies are tedious because there are so many combinations of molecules positions reaction sites etc.



(Tässä on lainattu kuvia Timo Weckmannin kandytyöstä.)

One usually assumes that the adsorption and diffusion barriers are small compared to the reaction barriers. The calculations are usually done a low coverages. This is not so great approximation

but it simplifies the calculations a lot. Also one need to keep in mind that there usually are several consecutive reactions.

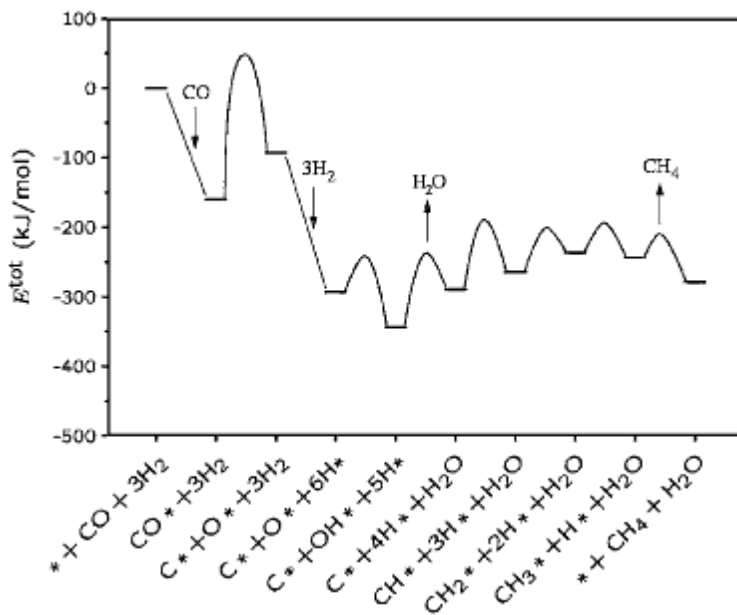
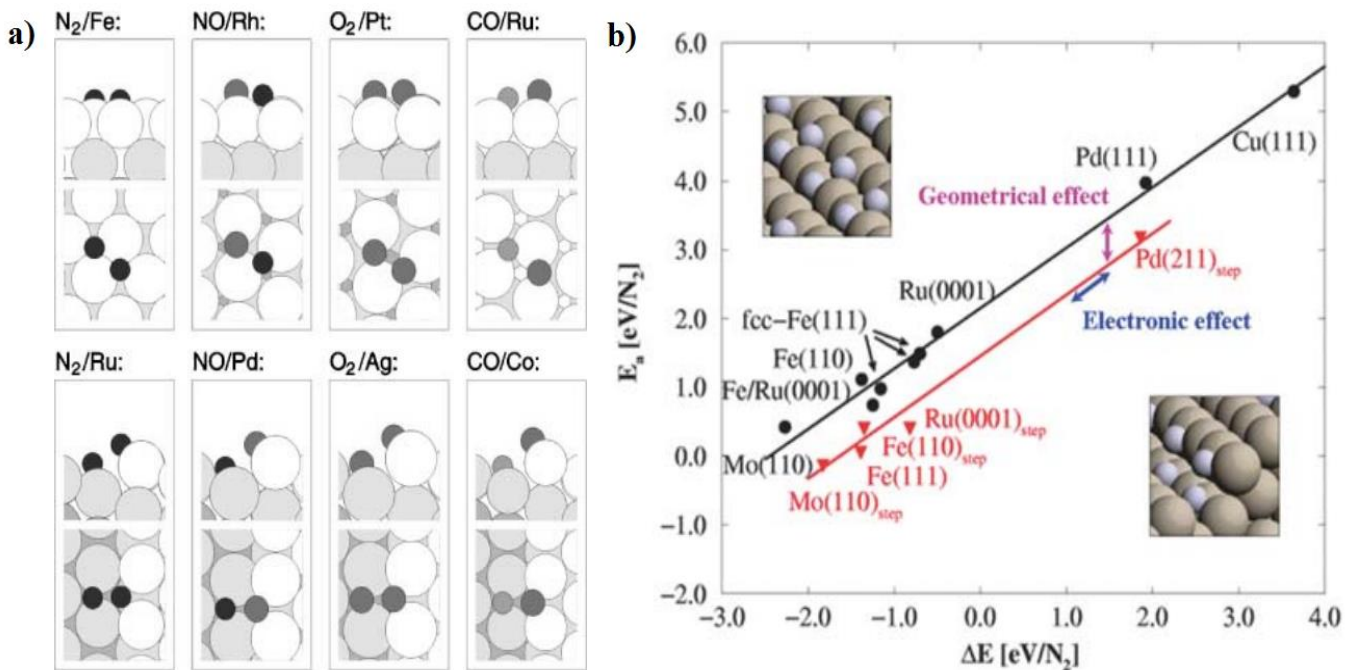


Figure: CO hydrogenation to methane

In the next figure a) describe the transition states of dissociation of N₂, NO, O₂ and CO on different flat and stepped surfaces. In figure b) is the N₂ dissociation barrier with respect of the N₂ reaction energy. Note that the points fit rather well to a line. Also the barriers on the stepped surfaces are smaller.



Source: Figure a) 1. J. K. Nørskov, et al, *Universality in heterogeneous catalysis*, *J. Cat.*, 209, 2002, Fig. b) J. K. Nørskov, et al. *The nature of the active site in heterogeneous metal catalysis*, *Chem. Soc. Rev.*, Vol 37, 2008

This linear behavior is so called Brønsted-Evans-Polanyi (BEP) linear reaction energy relation. It says that in **similar reactions** the activation energy depend linearly of the reaction energy:

$$E_a = \alpha\Delta E + \beta$$

The key assumption in the BEP is that the transition states are same. Why this relation is useful? The reaction energy calculations are much easier than the barrier calculations. So if the BEP assumption are valid the screening of good catalytic sites can be done efficiently

Volcano plot

The volcano plot or Sabatier principle are simple and very powerful concepts for understanding almost any catalytic reactions. The rationale is simple: if the catalyst bound the reactants too weakly it is not a good catalyst since nothing happens. On the other hand if the catalyst bound the reactant too strongly it is not good either since the many of the barriers (diffusion and desorption) will increase. This is a bit odd if we think this from the point of the BEP relation. One would think that catalyst that have the lowest reaction barrier would be the best. That would be true if the other steps will not grow higher but often they do. So the best real catalyst have medium binding energy. This the Volcano plot.

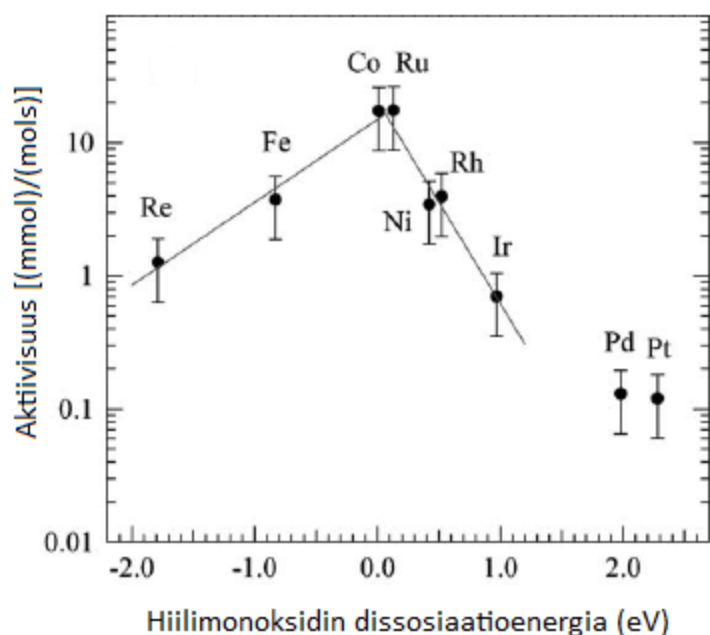


Figure: Activity of the CO methanation reaction.
(Tämä on lainattu Niko Holmbergin kandityöstä)

The activity can be expressed also with two variables. Below is the CO oxidation activity plotted as function of CO and O binding energies.

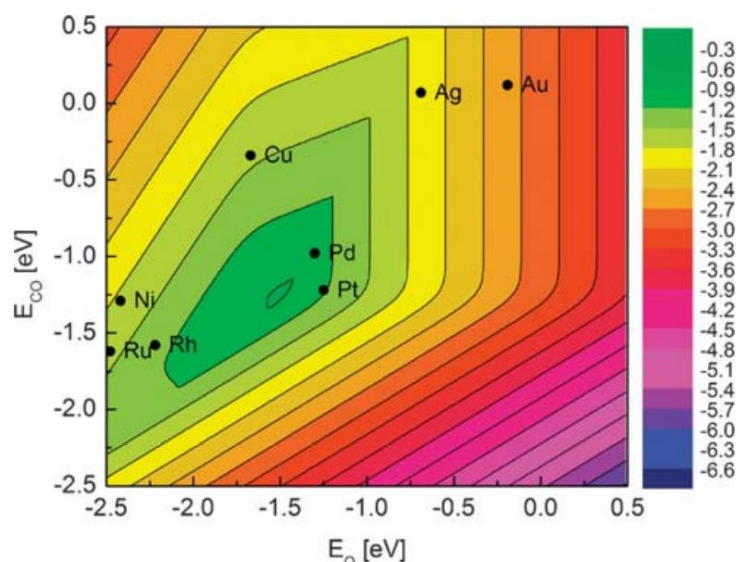
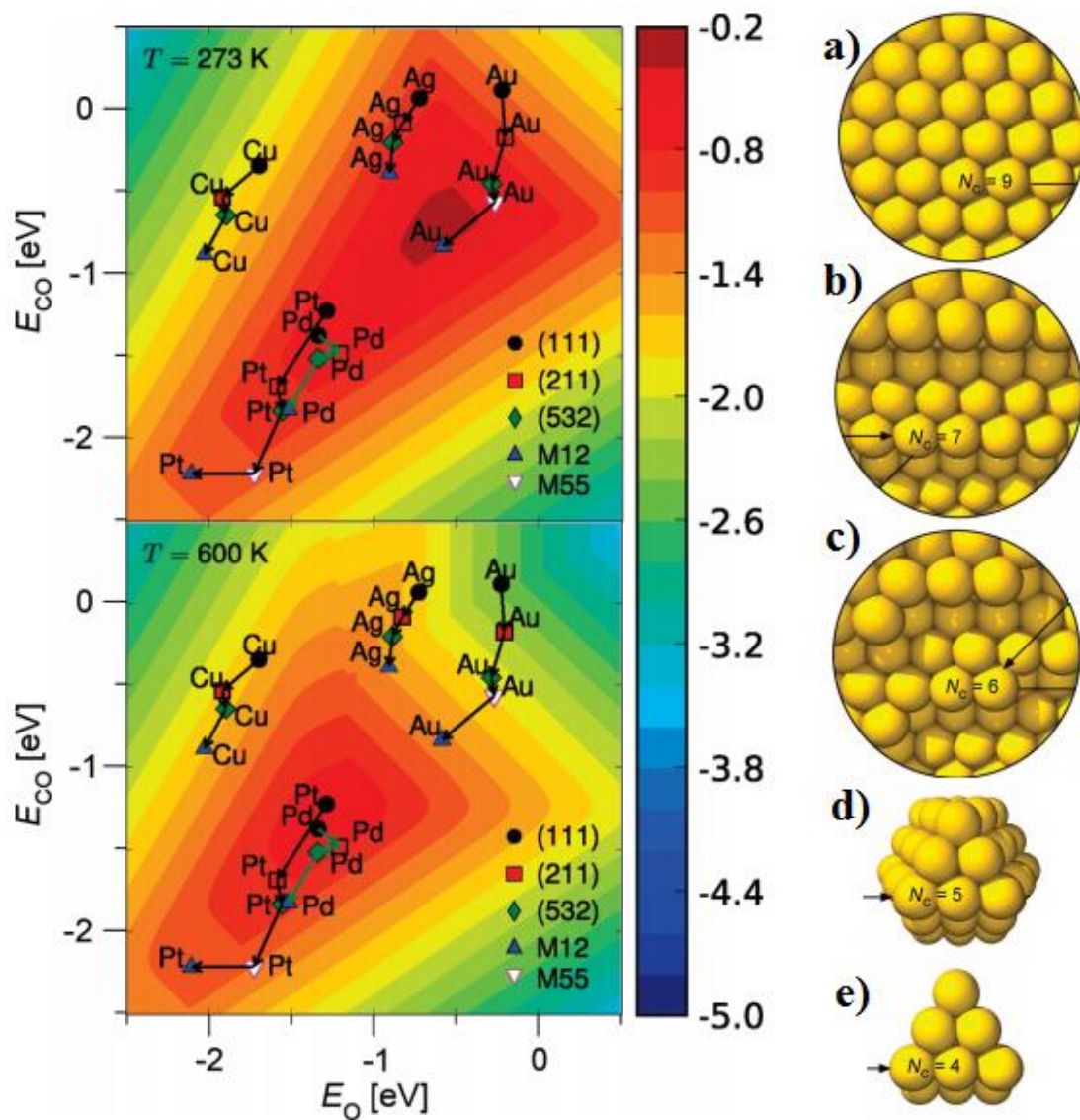


Figure CO oxidation. The $T = 600 \text{ K}$, $P(\text{O}_2) = 0,33 \text{ bar}$, $P(\text{CO}) = 0,67 \text{ bar}$. Source: H. Falsig, et al, *Trends in the catalytic CO oxidation activity of nanoparticles*, *Ang. Chem.*, 47, 2008, 4835-4839.

Next a very detailed study of CO oxidation on several Cu, Ag, Au, Pt, and Pd surface and on small clusters with two different temperatures (273 and 600 K). All these metal have FCC bulk structure.

At high temperature the Pt and Pd are the best catalysts, but at low temperature the Au₁₂ cluster is the best catalyst. (this is a bit artificial since the Au₁₂ cluster is rather unstable and it will dissociate rather quickly. The complexity of the surfaces increases: FCC(111) is a smooth surface, (211) is a stepped surface, (532) is a stepped and tilted surface. The 12 atom cluster have a very open structure and M55 cluster is a bit more compact. The reported value is the lowest barrier. There are several other reaction paths and I do not think they have been included to the study.



Source: T. Jiang, et al, *Trends in CO oxidation rates for metal nanoparticles and close-packed, stepped and kinked surfaces*, J. of Phys. Chem., 113, 2009, 10548-10553.

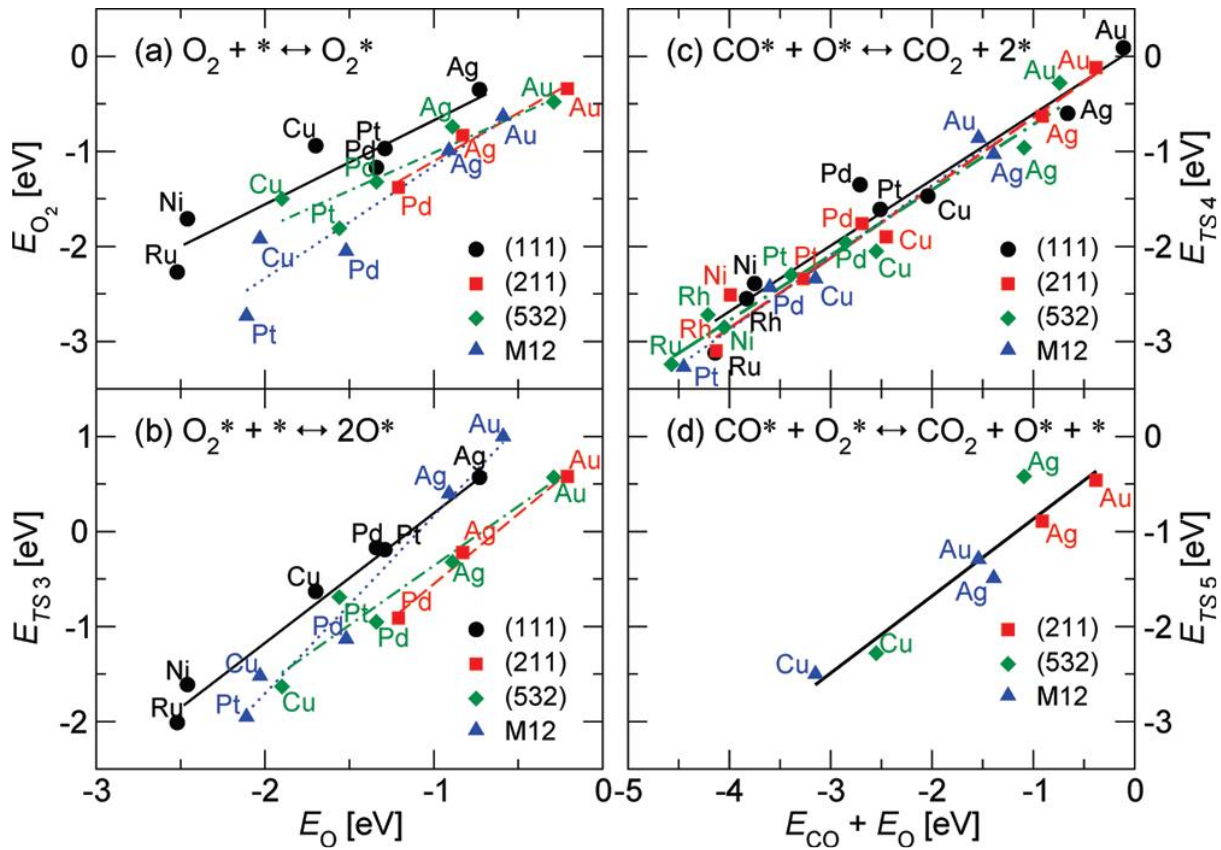


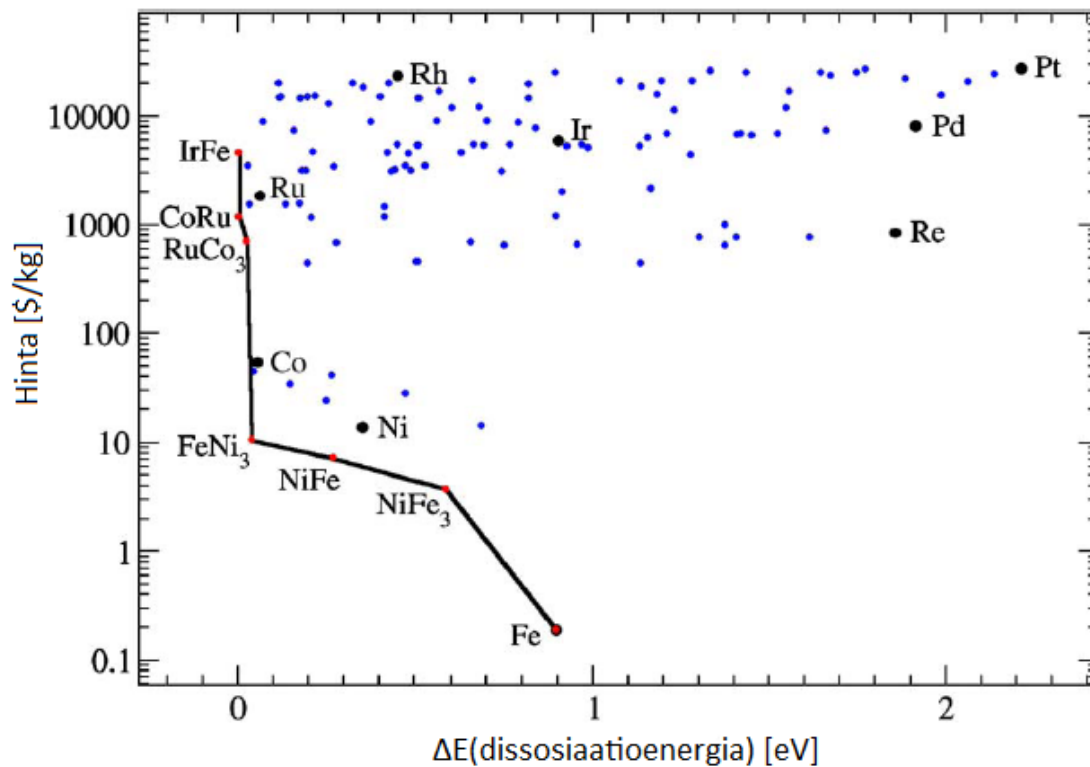
Figure 2. The scaling and BEP relations for (111) surfaces (b, s [black]), (211) surfaces (9, - - - [red]), (532) surfaces ([, - - - [green]), and M12 clusters (2, · · · [blue]). (a) The scaling of the O₂ adsorption energy E_{O_2} with the O adsorption energy E_O . (b) Calculated transition state energies for O₂ dissociation E_{TS3} (R3) as a function of O adsorption energy E_O . (c) Calculated transition state energies for adsorbed CO reacting with adsorbed O E_{TS4} (R4) as a function of the sum of the O and CO adsorption energies, $E_O + E_{CO}$. (d) Calculated transition state energies for adsorbed CO reacting with adsorbed O₂ E_{TS5} (R5) as a function of the sum of the O and CO adsorption energies, $E_O + E_{CO}$, with surface averaged BEP relation (s).

The BEP relations of the above paper

Catalyst optimization

Computationally one can find new catalyst but in the case of pure metals the good catalysts are almost always known. So the computational approach is not so useful but there are a huge amount of potential mixed metal catalysts. In this field the computational approach can be very useful. There are enormous amount of compounds and their screening for even a single reaction is demanding. On the other hand the computations are also demanding since one need to model the how the metals are ordered (including the surface enrichment) and after that there are several reaction barriers to be computed. In most of such screening calculations the PEB relation and volcano plot are used heavily.

As an example: a methanation reaction in which Ni is used a catalyst. 117 Ni, Pt, Pd, Co, Rh, Ir, Fe, Ru and Re mixtures has been studied computationally. Note that the black dots are ab initio computations and the blue dots are extrapolated. In the y-axis is the price of the catalysts.



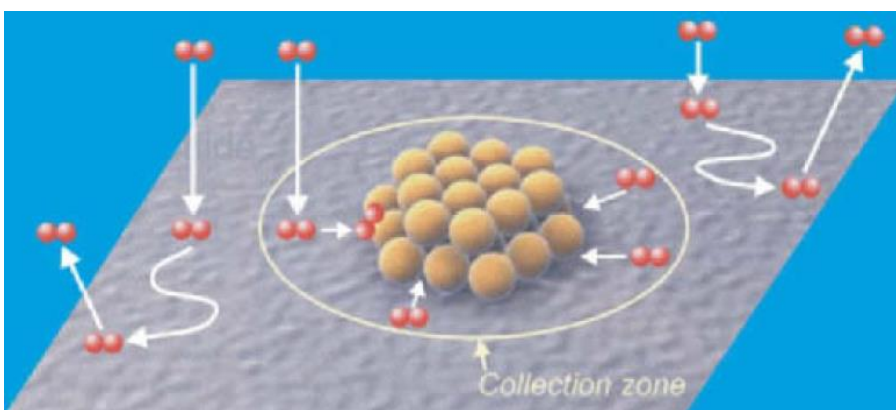
Lähde:

From the picture we can see that the NiFe mixtures are better catalysts compared to the pure Ni. In laboratory the NiFe mixtures are also better but the durability of the mixtures are not very good.

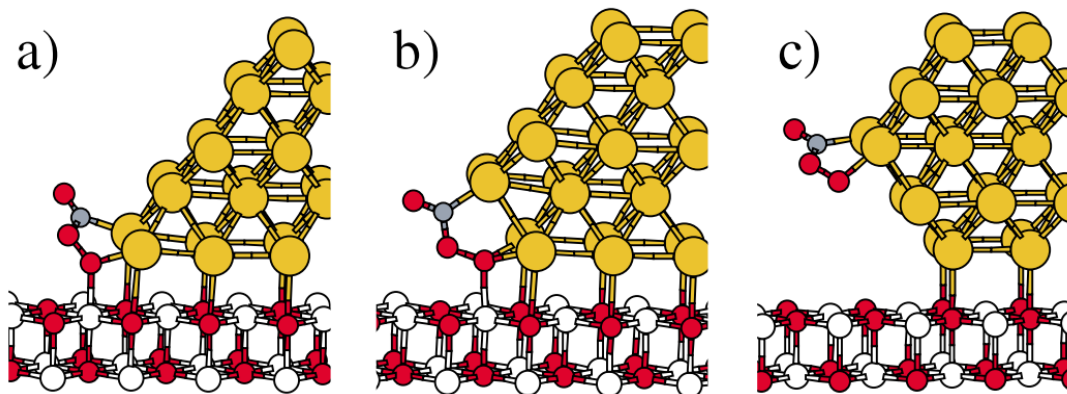
General comments: The computations can reveal a lot details of the catalytic reactions. One can even predict new potential catalyst using computations. Still the theoretically predicted catalyst need to be tested, first in laboratory scale and then on pilot scale. There are many issues that are hard to include in the modelling. These include the poisoning of the catalyst. The poisoning means that some compound, like CO, S, O etc., will bind to the surface so strongly that it prevent the catalytic reaction. Another issue it he durability of the catalyst. The catalyst can break down or it can oxidize. Especially the latter is very difficult to study at atomic level.

Catalyst and support

The catalyst is almost always on some support. The support is often some rather strong oxide like Al_2O_3 , MgO , TiO_2 . Sometimes the support need to conduct electrons so an amorphous graphite is used. Often to support is assumed not to affect the catalytic reaction. This is usually not true. It is known that the catalytic activity depend on the support. There are several factors that might change the reactions. The reactants can land on the support and diffuse to the catalyst. In this case the diffusion on support will affect the reactivity. Also the edge of the catalyst particle can be more (or less) active than the actual catalyst.



Example: CO oxidation on Au cluster on MgO interphase. There are several models of the interphase. The structure is the most active.



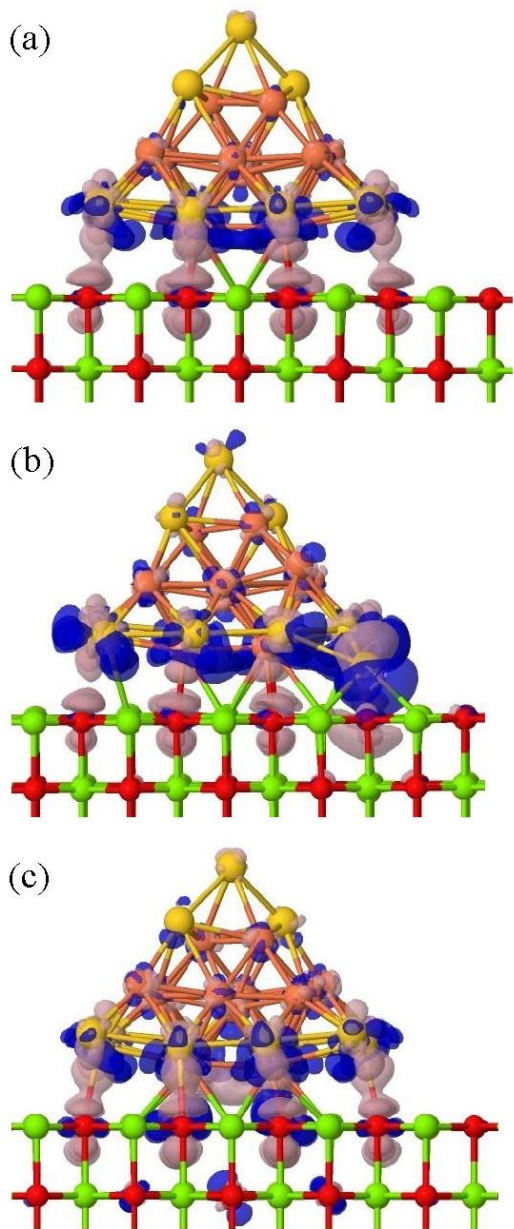
Lähde: L. M. Molina ja B. Hammer, *Active Role of Oxide Support during CO Oxidation at Au/MgO*, Phys. Rev. Lett., 90, 206102.

In the case of the oxidation reactions and if the support is an oxide, the support can store and release oxygen.

Overall the real catalyst is a very complex system.

Li, Ma, Kari Laasonen and Jaakko Akola, submitted to J. Phys. Chem C. (2017)

Density functional simulations have been performed for $\text{Au}_{15}\text{Cu}_{15}$ clusters on $\text{MgO}(100)$ supports to probe their catalytic activity for CO oxidation.



Li, Ma, Kari Laasonen and Jaakko Akola, submitted to J. Phys. Chem C. (2017)

Density functional simulations have been performed for $\text{Au}_7\text{Cu}_{23}$ and $\text{Au}_{23}\text{Cu}_7$ clusters on $\text{MgO}(100)$ supports to probe their catalytic activity for CO oxidation.

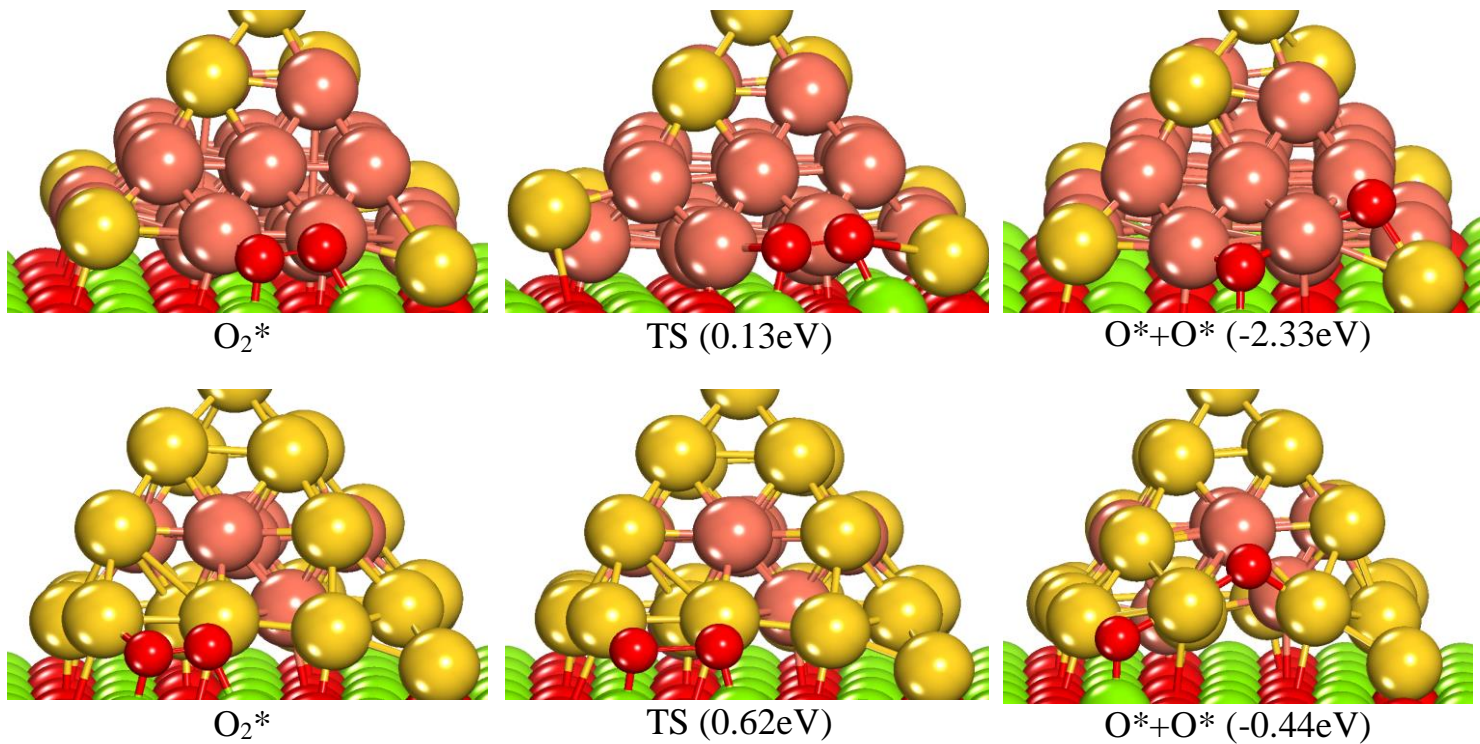


Figure 4

Structures of the initial state (IS), transition state (TS), and final state (FS) of the lowest identified pathways for $O_2 \rightarrow O + O$ on $Au_7Cu_{23}/MgO(100)$ and $Au_{23}Cu_7/MgO(100)$ with the F-center and the energy changes with respect to the IS. The symbol '*' refers to the atom or molecule being adsorbed on the cluster.