

Theoretical study of the geometrical, electronic and catalytic properties of metal clusters and nanoparticles.



INSTITUTO DE
TECNOLOGÍA
QUÍMICA



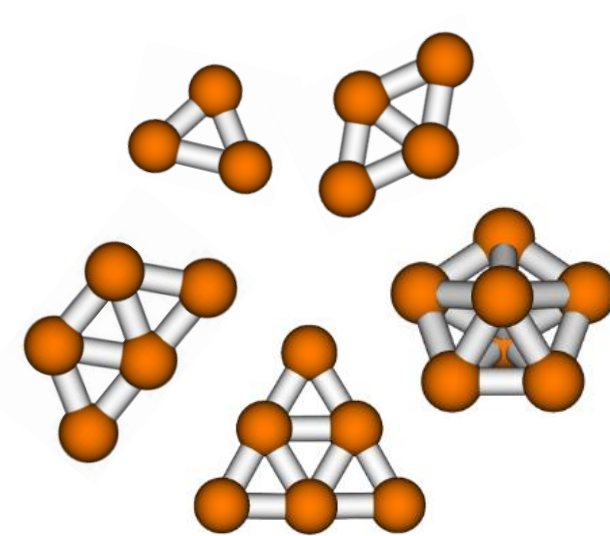
Doctorado en Química Sostenible
Estefanía Fernández Villanueva, esfervi1@doctor.upv.es

Director de tesis: Mercedes Boronat, boronat@itq.upv.es

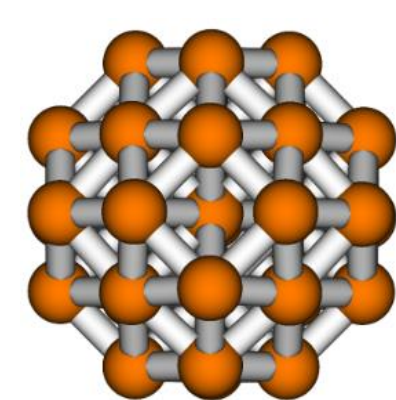
Instituto de Tecnología química, UPV-CSIC, Universidad Politécnica de Valencia – Consejo Superior de Investigaciones Científicas,
Avda. de los Naranjos s/n, 46022 Valencia, Spain

Objective

To study the reactivity of metal clusters and nanoparticles of increasing size and different structure by means of a theoretical modelling of the systems, in order to help in the design of new catalysts.



clusters
< 1 nm



nanoparticles
1 – 5 nm

Background and motivation

Transition metal nanoparticles with a diameter between 1 and 5 nm have improved catalytic properties with respect to bulk metals. Subnanometric clusters have been also identified as responsible for the catalytic activity in some important reactions.¹⁻⁴

The interest in understanding the causes for this different behavior and the possibility of discovering new effective catalysts for different reactions is the main motivation of this thesis.

[1] Science 2008, 321, 1331–1332 [2] Nature Mat. 2009, 8, 213 [3] Science 2012, 338, 1452 [4] Nat. Chem. 2013, 5, 775

Computational details

Based on atom-centered gaussian orbitals DFT- Gaussian 09.

- Hybrid functional B3PW91 with Def2-TZVP basis set for Cu atoms and 6-311+G(d,p) basis set for O atoms.
- Atomic charges and MO distributions: NBO.
- Transition states: PES scan.

Plane-wave based periodic DFT – VASP code.

- Clusters placed in a 20x20x20 Å cubic cell.
- GGA PW91 functional (labelled p-PW91)
- Cutoff = 450 eV, PAW, Γ k-point.
- Transition states: DIMER

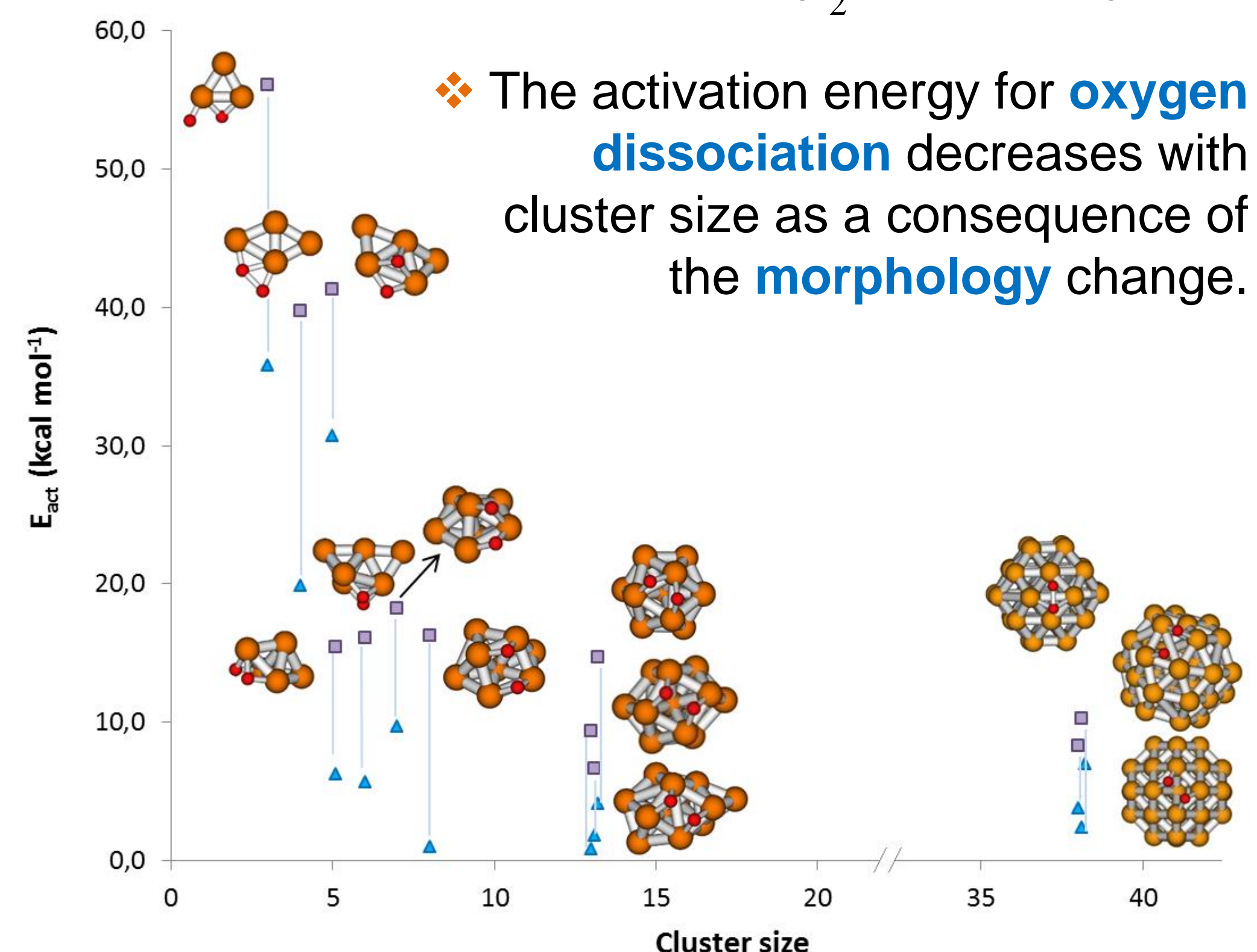
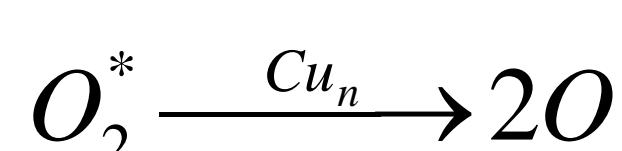
Research stages

There will be several different processes to study, but the main research stages will commonly involve studying:

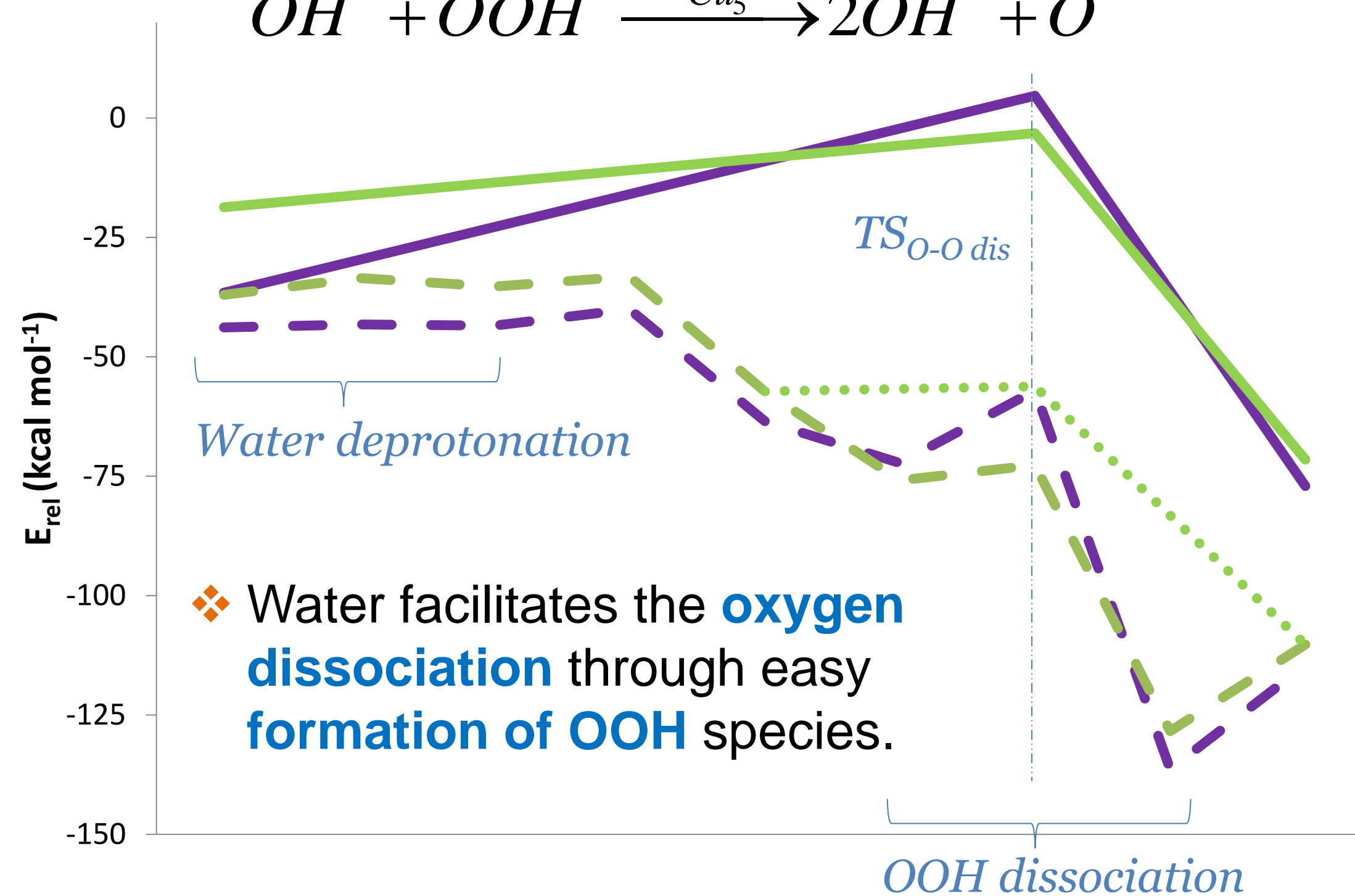
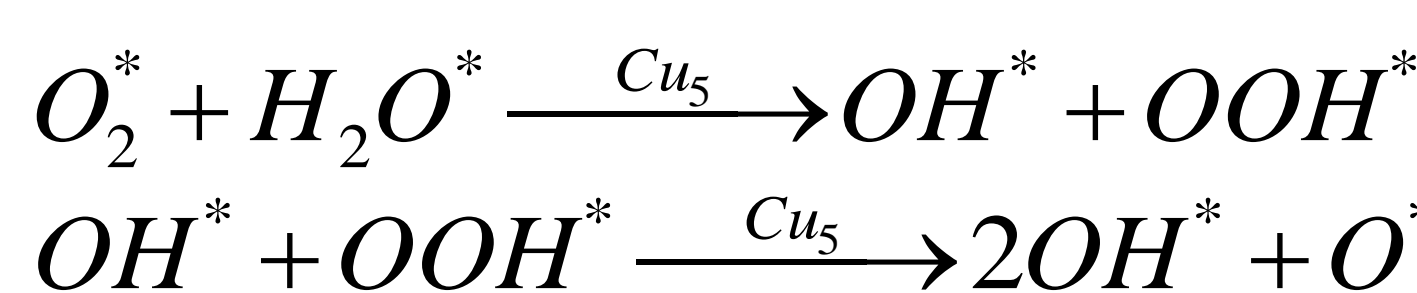
- The most stable structures of the clusters or nanoparticles alone.
- The different adsorption patterns of the molecules on the most stable isomer of the cluster or nanoparticle.
- The mechanism of the reaction, in order to assess the catalytic activity of the clusters or nanoparticles in that reaction.

First results

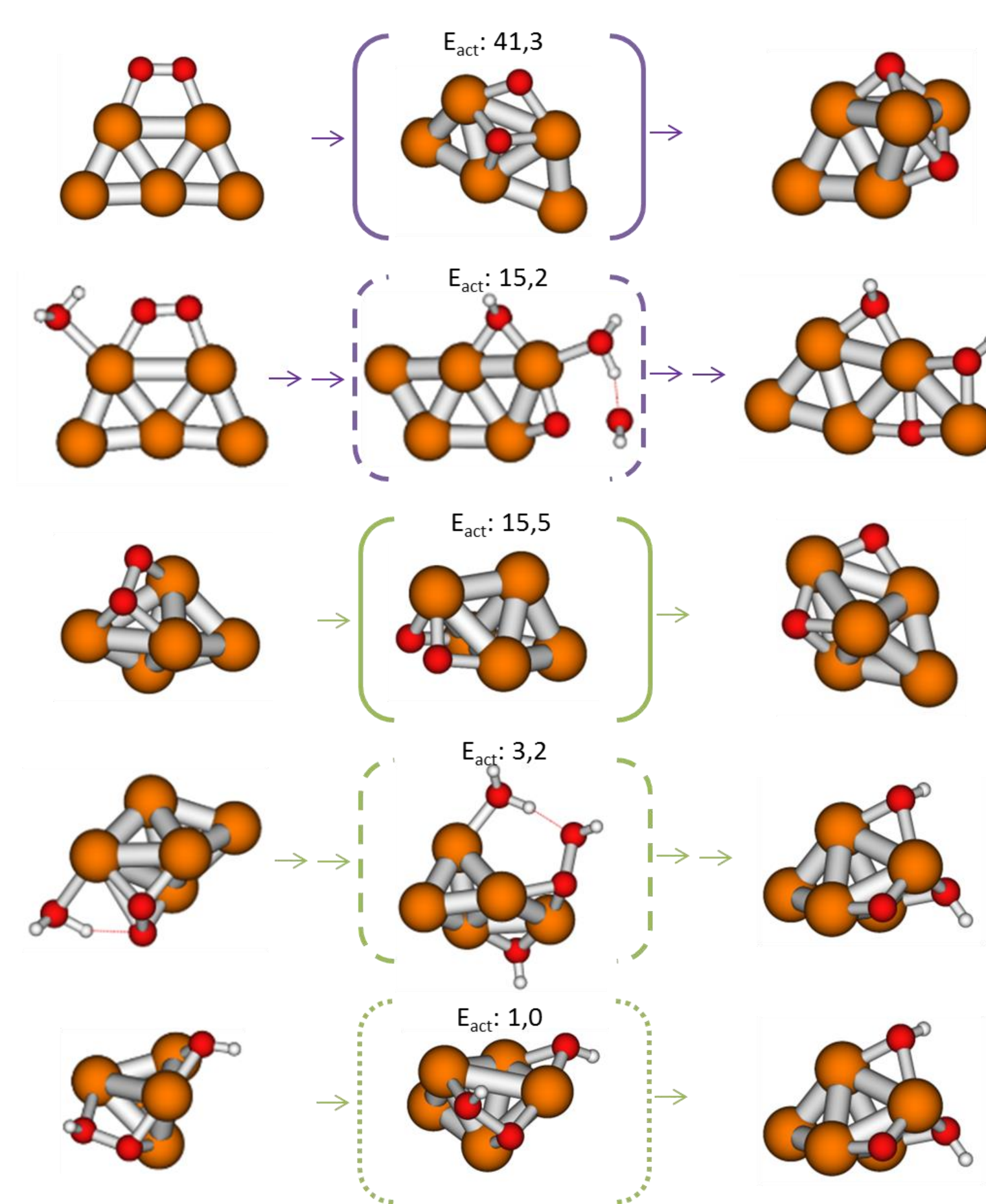
Oxygen dissociation in absence and presence of water



- The activation energy for oxygen dissociation decreases with cluster size as a consequence of the morphology change.



- Water facilitates the oxygen dissociation through easy formation of OOH species.



Future work

Similar stages at the B3PW91/Def2-TZVP level will be followed with other reactions:

- CO oxidation with oxygen: $CO + \frac{1}{2} O_2 \xrightarrow{Cu_n} CO_2$
- Water Gas Shift reaction (WGS): $CO + H_2O \xrightarrow{Cu_n} CO_2 + H_2$
- Propene epoxidation:

Spectra simulation is meant to be done and compared with experimental results if the latter are available. Larger systems will also be studied with the p-PW91 method. Finally, other transition metals or bimetallic systems will be included.

Possible applications

The practical application of this thesis relies upon the discovering and characterization of new catalysts based on small clusters of transition metals and their properties. Hopefully, the new catalysts found will be either cheaper, more efficient, more selective or more environmentally friendly than those currently used for the corresponding reaction, and thus will have potential industrial applicability.

At the very least, this work will provide some insight on the behavior of transition metal clusters and nanoparticles and information that may aid in their future synthesis.