TÍTULO: Theoretical study of the geometrical, electronic and catalytic properties of metal clusters and nanoparticles.
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Resumen de presentación

Transition metal nanoparticles with diameter between 1 and 5 nm have improved catalytic properties with respect to bulk metals[1,2]. Furthermore, subnanometric clusters have also been found to be responsible for the catalityc activity in some important reactions[3,4]. This different size-based behavior has no straightforward cause, but these findings made the research of transition metals clusters and nanoparticles become a very interesting subject industrially, due to the possible discovery of new catalysts.

Indeed, the general aim of the thesis is to study the reactivity of transition metal clusters and nanoparticles of increasing size by means of a theoretical modelling of the systems, in order to help in the design of new catalysts.

Copper nanoparticles catalyze important industrial processes[5-6], and recently small clusters have also shown catalytic activity[7]. In addition, copper has the industrial advantage of being a cheap resource. Due to all this, we chose copper to start our investigation on transition metal clusters.

However, transition metal systems are not easy to handle computationally. In fact, the appropriate methods to use are only applicable to the smallest systems, and one has to switch to a completely different theoretical method when systems get larger. Due to this, a first difficult goal was to stablish an appropriate methodology to be able to study systems of increasing size and, hopefully, be able to compare their results.

The next research stages consist in the study of the clusters isomers of different sizes and their interaction with common molecules. More specifically, they include:

- ✓ The most stable structures of neutral clusters per size.
- ✓ The different adsorption patterns of common molecules on the most stable isomer per cluster size.
- ✓ The catalytic activity of the clusters in certain reactions of interest, which in turn includes:
    - Transition states (TS) studies through Potential Energy Surface scans.
        - Activation energy (E_{act}) evaluation as the difference between TS and reactants: $E_{act} = E_{TS} - E_R$.

- Reaction products (P) calculations.
    - Reaction energy (E_{reac}) evaluation as the difference between P and reactants: $E_{reac} = E_P - E_R$.

We started with the study of the adsorption and dissociation of the oxygen molecule on the copper clusters. In the future, similar stages are to be followed with other reactions such as:

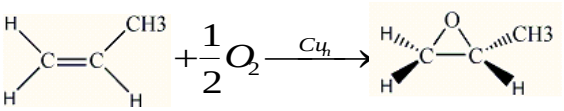
- CO oxidation with oxygen

$$CO + \frac{1}{2}O_2 \xrightarrow{Cu_n} CO_2$$

- Water Gas Shift reaction (WGS)

$$CO + H_2O \xrightarrow{Cu_n} CO_2 + H_2$$

- Propene epoxidation



In addition, larger systems will be studied and other transition metals or bimetallic systems will be included.

Finally, spectra simulation is meant to be done and compared with experimental results if the latter are available.

As a matter of fact, the future collaboration with experimental groups at the ITQ will provide further understanding of the subject. Indeed, the synthesis of small clusters and nanoparticles is not easy and the attempts are costly, thus remarking the importance of theoretical studies, which can explore many more possibilities and either suggest best candidates or discard others, as well as explain the reasons underneath.

The ultimate goal of this theoretical research, therefore, is to assist in the design of new catalysts, which hopefully 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.

References

[1] *J. Catal*. 1993, 144, 175–192.
[2] *J. Catal*. 2011, 278, 50–58
[3] *Nature Chemistry* 2013, *5*, 775.
[4] *PCCP* 2014, *16*, 26600.
[5] *Angewandte Chemie-International Edition* 2005, *44*, 7978.
[6] *Nature* 2014, *508*, 504
[7] *Acs Catalysis* 2013, *3*, 182

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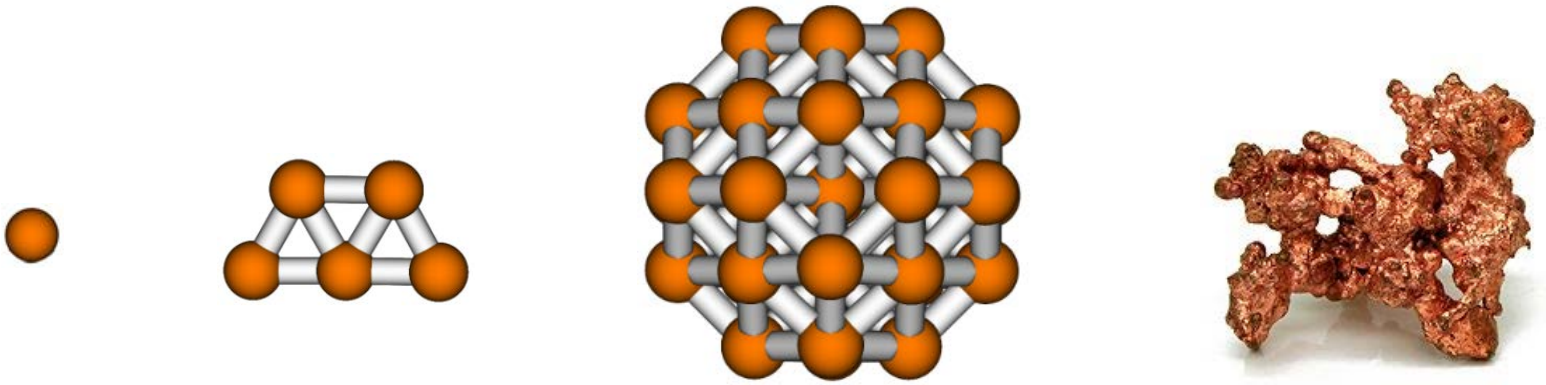
Thesis main goal

To study the reactivity of transition metal (TM) 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**.



Cu atom — cluster — nanoparticle — bulk

< 1 nm — *1 – 5 nm* — *Increasing size*

Background and motivation

- **TM nanoparticles (1-5 nm)** are better catalysts than bulk:
  - CO oxidation of Au supported on TiO_2, α-Fe_2O_3 and Co_3O_4 increases when particle size is < 4nm[1].
  - Alcohol oxidation over Au/MgO is maximum at ~3nm particle size[2].

- **Subnanometric clusters (<1nm)** also catalyze important reactions:
  - Thiophenol (Ph-SH) oxidation to disulfide ($(S\text{-}Ph)_2$) is maximum with Au clusters with 5-10 atoms[3].
  - Subnanometric Ag clusters stabilize O_2 and easily form hydroperoxides as reaction intermediates, while smaller clusters (n=3, 5) do not[4].

❖ The causes for these differences vary from one reaction to another and are not clear. **Understanding them is key for the synthesis of new catalysts**.

❖ Similarly, **copper** nanoparticles **catalyze important industrial processes** such as alcohol syntheis[5] or the CO electroreduction to liquid fuels[6] , and recently small clusters have also shown catalytic activity[7].
In addition, copper has the industrial advantage of being a **cheap resource**.

[1] *J. Catal*. 1993, 144, 175–192. [2] *J. Catal*. 2011, 278, 50–58 [3] *Nature Chemistry* **2013**, *5*, 775. [4] *PCCP* **2014**, *16*, 26600.
[5] *Angewandte Chemie-International Edition* **2005**, *44*, 7978. [6] *Nature* **2014**, *508*, 504 [7] *Acs Catalysis* **2013**, *3*, 182

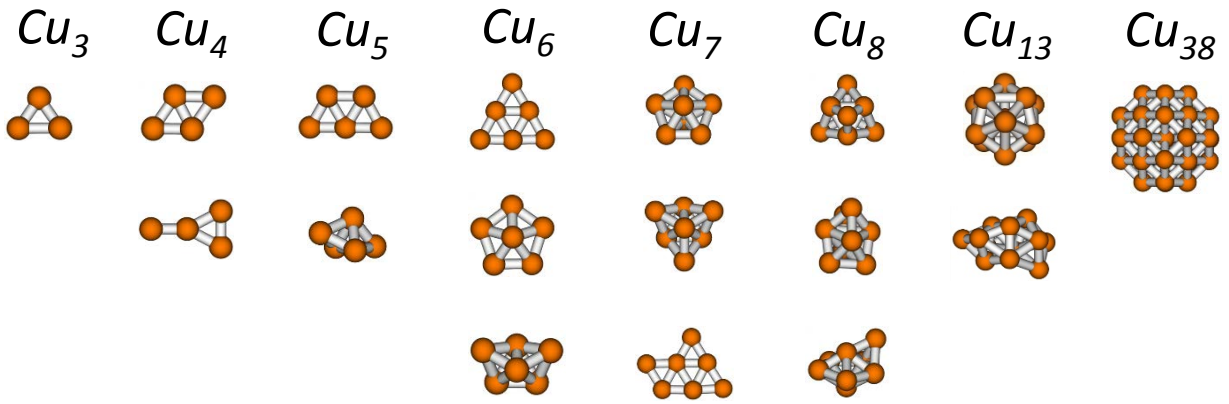
Research stages

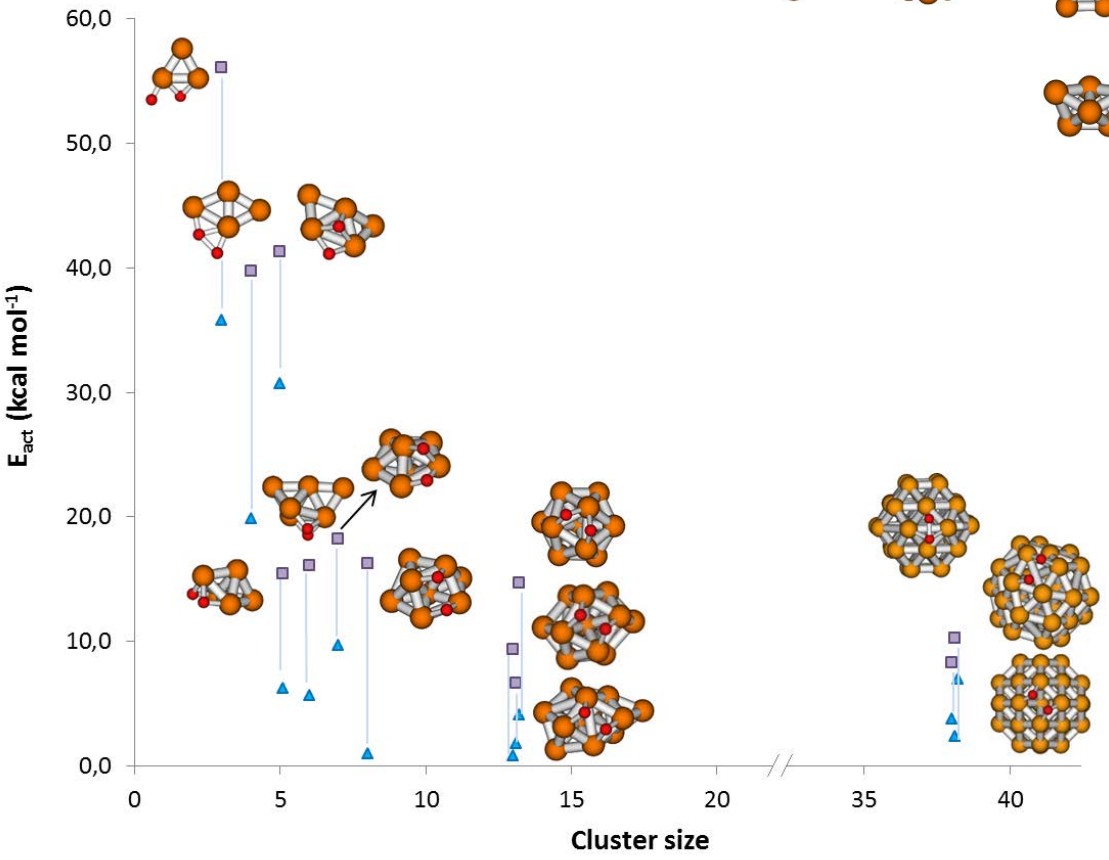
A first goal is to **stablish an appropriate methodology** and then, in general, to study transition metal systems of increasing size computationally:

- ✓ The **most stable structures of neutral clusters** per size, starting with Cu.
- ✓ The **different adsorption patterns of common molecules** on the most stable isomer per cluster size, starting with O_2.
- ✓ The **catalytic activity** of the clusters in certain reactions of interest, starting with O_2 dissociation, which includes:
  - o Transition state (TS) study through Potential Energy Surface scans.
    - **Activation energy** (E_{act}) evaluation as the difference between TS and reactants: $E_{act} = E_{TS} - E_R$.
  - o Reaction products (P) calculations.
    - **Reaction energy** (E_{reac}) evaluation as the difference between P and reactants: $E_{reac} = E_P - E_R$.

Models and first results

- Neutral copper clusters are planar up to n=6.





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

Future work

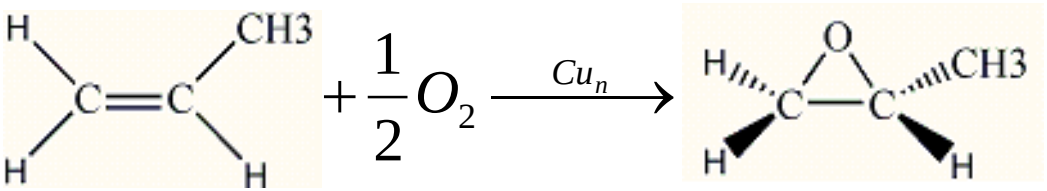
- **Similar stages** will be followed at the B3PW91/Def2-TZVP level with **other reactions**:
  - CO oxidation with oxygen:

$$CO + \frac{1}{2}O_2 \xrightarrow{Cu_n} CO_2$$

  - Water Gas Shift reaction (WGS):

$$CO + H_2O \xrightarrow{Cu_n} CO_2 + H_2$$

  - Propene epoxidation:



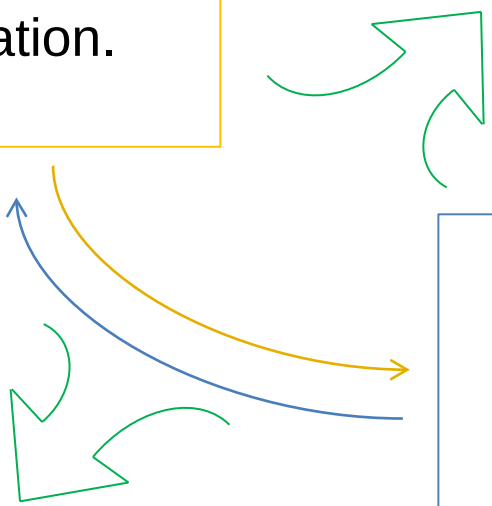
- **Larger systems** will also be studied with the p-PW91 method.
- **Other transition metals or bimetallic systems** will be included.
- **Spectra simulation** is meant to be done and compared with experimental results if the latter are available.

Collaboration and applications

Experimentally:

- Synthesis attempts.
- Spectroscopic characterization.
- Catalyst evaluation.

New or Improved Catalysts



Theoretically:

- Structure control, but many more possibilities.
- Characterization.
- Catalyst evaluation.

Further understanding of results on both sides.

Thank you for your attention!

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

Doctorado en Química Sostenible

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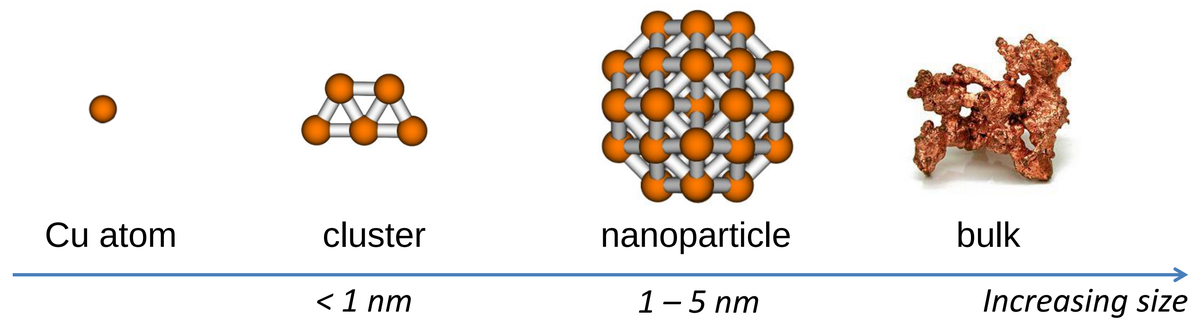


Background and motivation

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

Research stages

- ✓ A first goal is to **stablish an appropriate methodology** to study transition metal systems of increasing size computationally, specifically:
- ✓ The **most stable structures of neutral clusters** per size.
- ✓ The **different adsorption patterns of common molecules** on the most stable isomer per cluster size.
- ✓ The **catalytic activity** of the clusters in certain reactions of interest.

Computational details

The methods employed are based on the Density Functional Theory:

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

- Hybrid functional B3PW91 with **6-311+G(d,p)**, **LANL2DZ** and **Def2-TZVP** basis sets and **BPW91** functional with Def2-TZVP basis set (Cu atoms). 6-311+G(d,p) basis set for O atoms.
- Atomic charges and MO distributions: NBO.
- Transition states: PES scan.

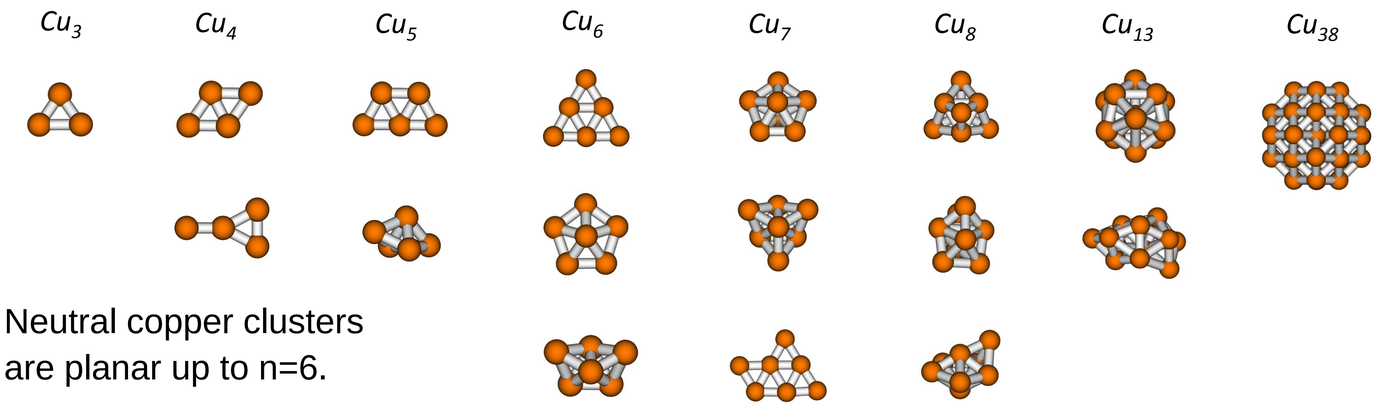
Plane-wave based periodic DFT – VASP code.

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

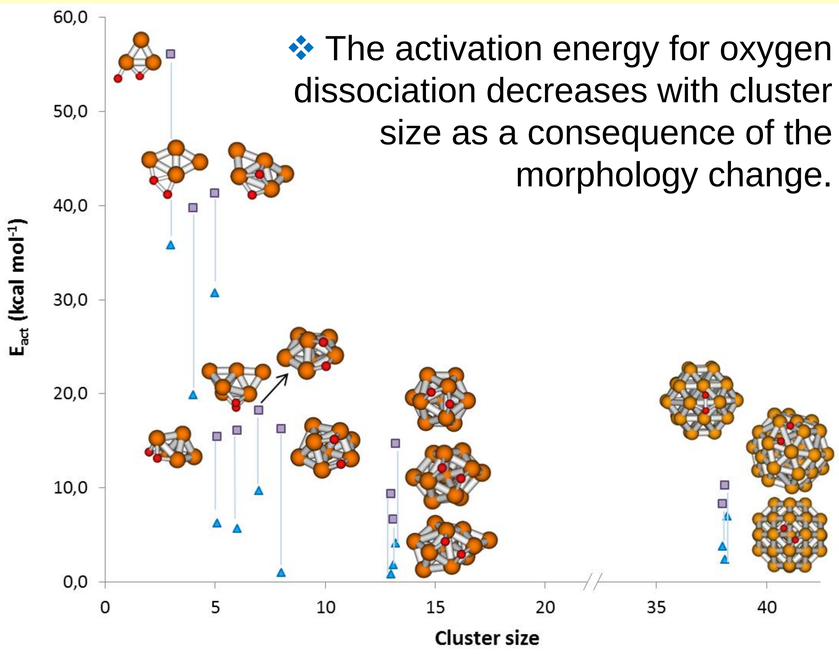
Models and first results

➢ In order to fulfill the previous research stages, we selected a variety of computational methods to study copper clusters of size n=3-8, 13 and 38 along with the adsorption and dissociation of one oxygen molecule on them.

Different isomers per cluster size are found with energies close to the groundstate structures:



❖ Neutral copper clusters are planar up to n=6.



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

Future work

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

- CO oxidation with oxygen: $CO + \frac{1}{2}O_2 \xrightarrow{Cu_n} CO_2$
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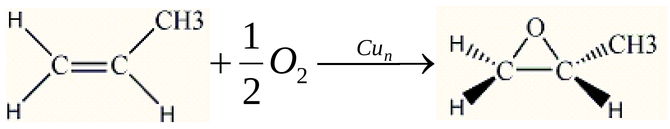

Spectra simulation is meant to be done and compared with experimental results if the latter are available. **Larger systems** will also be studied with the p-PW91 method. Finally, **other transition metals or bimetallic systems** will be included.

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.**

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