Subnanometer catalysts to face the shortage of precious raw materials: insights from numerical simulations

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The usage of subnanometer catalysts directly tackles the shortage of raw materials, because a large active area is available at a price of a small amount of material. Metal nanoclusters are extremely important in the transition to new energy resources as well as in high-efficiency catalytic reactions. Currently, the main **bottleneck** in the practical use of few-atom clusters lies in their reduced stability at the typical operating conditions: upon annealing and/or gas exposure, **clusters tend usually to sinter, or agglomerate**, leading to a dramatic decrease in their catalytic performance. It is therefore **important i) to investigate the cluster stability and ii) to explore their catalytic properties in different conditions.** A key mechanism to stabilise small clusters is the use of a suitable support. Graphene grown on a Ni substrate is a promising system, since it intrinsically provides possible anchoring sites for clusters [1]; when graphene is supported on (100) Ni facets, a moiré structure is formed, offering a templating effect that may affect sintering (fig. 1) [2].

We will focus on **Cobalt clusters**, whose behaviour on different Nickel surfaces (bare or carbie covered) has been recently studied by our group (fig. 2) [3]. In particular, the PhD candidate should afford the investigation of Co nanostructures on proper substrates through models and quantum mechanical ab-initio simulations based on Density Functional Theory (DFT), in continuous comparison with experiments that will be performed by C. Africh and coworkers at the CNR-IOM Lab in Basovizza. An external collaboration with a group at the University of Còrdoba (Argentina) is planned, to complement the local expertise with their experience in classical force-field potentials and molecular dynamics, to expand the investigation to clusters of larger size and to their mobility and possible sintering effects with the temperature. The collaboration has been already successful in the study of defects and of the kinetics involved in graphene grown process on Ni(111) [4].

A first part of the project will be devoted to study the behavior of **Cobalt clusters on the support: a graphene monolayer on (111) and (100) Nickel surfaces**. Graphene almost perfectly matches with the (111) surface and is planar but on the (100) surface the lattice mismatch leads to corrugation and moiré patterns (fig. 2) [2]. DFT has been already successfully used to simulate some selected graphene/nickel moiré structures that can host Cobalt nanoclusters of different size. Preliminary DFT calculations suggest that Co does not adsorb with the same strength on different non-equivalent graphene sites. The corrugation-induced anisotropy is expected to determine preferential adsorption sites, size and shape of Co nanoaggregates.

A second part of the project is devoted to clarify the effect of the **exposure of these clusters to gas molecules**, as well as the atomistic mechanisms of simple reactions. DFT calculations (on computationally affordable reduced systems) will be performed on the most stable structures found in the previous step, to study the adsorption and reaction of small molecules. These high-level calculations will allow us to analyse the chemical and catalytic activity of the supported nanoclusters. In particular, we are interested in obtaining the adsorption energies and sites, and also reaction paths for molecular dissociation.

Since large supercells could be necessary to describe moiré structures [5], we will apply for *grants* to access high-performance computing resources in CINECA and other facilities.

Previous selected publication of the group, relevant for this project:

[1] Carnevali V. et al, *Nanoscale 11* (2019) 10358-10364

[2] Zou Z. et al, *Carbon* 130 (2018) 441-447

[3] Chesnyak V. et al, *Nanoscale 14* (2022) 3589-3598

[4] Patera L.L. et al, *Science 359* (2018) 1243-1246

[5] V. Carnevali et al., *Computational Materials Science 196* (2021) 110516

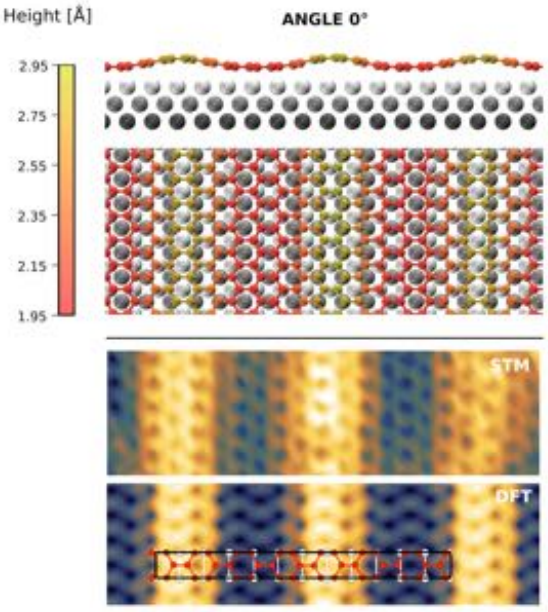

Fig. 1: Moirè structure formed by graphene on Ni(100), aligned along the zigzag direction: DFT optimized models, experimental scanning tunneling microscopy (STM) image and simulations. Adapted from [2].

Fig. 2: Summary of the behavior of Cobalt clusters with the temperature and with the modification of the support (from bare Ni surface to a carbide (Ni_2C) covered surface). [3]