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Interaction of carbon monoxide with Cu nanoclusters grown on alumina surface

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Summary. — The present work addresses the interaction of carbon monoxide with copper nanoclusters supported on an ultrathin alumina film grown on the $Ni_3Al(111)$ termination, acting as a template for a highly ordered nucleation. Through accurate quantum-mechanical calculations combined with experimental data, it has been found that the dissociation of carbon monoxide occurs at the copper nanoclusters, at variance with extended surfaces. The detailed mechanism is explained at the atomic level, unveiling the effects of cluster finite size, reconstruction, support, and carbon monoxide coverage. The small size of the nanoclusters allows to achieve an exceptionally high local concentration of molecules at the cluster surface, considerably higher than the saturation limit for the single crystal surfaces. The high coverage facilitates the dissociation of the molecules, accompanied by carbon incorporation into the particles. We discuss the possibility of using other transition metals for an optimal seeding of the supported nanoparticles. In agreement with empirical findings, Pd is confirmed to be the best choice for a highly ordered nucleation.

PACS 61.46.-w – Structure of nanoscale materials.
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1. – Introduction

Carbon monoxide is an important reactant in many industrial catalytic processes. Because of that, the chemistry of CO on different catalytic surfaces is a hot topic also in surface science experimental investigations, where the progress in microscopy and spectroscopy techniques both in ultra-high vacuum (UHV) environment and at higher pressures makes it possible to investigate the chemical reactions at the atomic level, and also in conditions that are closer to realistic ones.

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In particular, the CO dissociation is a fundamental step in many elementary sub-processes, such as, $e.g.$, in the Boudouard reaction, which converts carbon monoxide into carbon dioxide and atomic carbon ($2CO \rightarrow CO_2+C$). The direct CO dissociation process at single-crystal surfaces is strongly endothermic and very unfavourable: for instance, on Cu(111) the dissociated state with C and O atoms separately adsorbed is about $2\,eV$ higher with respect to the adsorbed CO molecule, whose binding energy to the surface is about $0.8\,eV$ [14]. The situation can be different at low coordination sites, such as those in defects or steps, that can act as efficient centers in heterogeneous catalysis.

Metal nanoparticles (NPs) show a very high concentration of edges and kinks. In general, they exhibit exceptional physical and chemical properties due to their size and high surface-to-volume ratio [1, 2]. For practical purposes, NPs must be grown on a substrate, which can play an important role in controlling their size and behaviour ($e.g.$ selectivity towards specific reactions) and in preventing sintering at high temperature. The synthesis of ordered arrays of well-defined equally sized NPs is therefore the goal of many efforts. To this purpose, ultrathin oxide films have been recently proposed as templates for the ordered growth of NPs through self-organization of adatoms upon chemical vapour deposition (CVD), exploiting the intrinsic properties of the substrate.

In order to unveil the catalytic effect of NPs on the CO dissociation process at the atomic-scale level, in this work we consider its interaction with Cu clusters supported on an alumina template grown on the Ni$_3$Al(111) termination as a model system, using accurate quantum-mechanical calculations corroborated by $in\ situ$ and $in\ operando$ spectroscopy measurements.

In the first part of this work we focus our attention on the seeding mechanism and the first stages of nucleation of NPs on Al$_2$O$_3$/Ni$_3$Al(111). We first consider the self-seeding and nucleation of Cu. Secondly, we investigate the seeding and nucleation process of various selected transition metals, giving a rationale for the different behaviour of the metallic species when deposited through CVD and in particular for the peculiarity of Pd [3-6]. The second part is devoted to the interaction of CO with Cu clusters, focusing on the energetics of the adsorption, direct dissociation followed by recombination with an Eley-Rideal mechanism, or, alternatively, a reaction through a Langmuir-Hinshelwood mechanism. The role of the finite size of the clusters is addressed comparing the results with the single crystal case. The effect of coverage, that can reach high values because of the curvature of the exposed surface of the NPs, is also discussed.

2. – Methods

The Al$_2$O$_3$ ultrathin film on Ni$_3$Al(111) has been obtained through oxidation of the clean Ni$_3$Al(111) surface under UHV conditions, following the protocol described in details in [7]. The structure of the extremely homogeneous and almost defect-free ultrathin alumina film has been precisely identified in previous works [8-11]. When imaged using scanning tunnelling microscopy, the alumina film shows two different appearances under different bias voltage, named as "dot" and "network" superstructures. The unit cell is a hexagonal big cell containing three defective sites that can act as anchoring sites for the nucleation of NPs: a "hole" that reaches the supporting metallic alloy and defines the "dot" sublattice, and two threefold sites that, together with the hole, define the "network" sublattice. The overall structure, used as input in the numerical simulations, is represented in fig. 1.

Calculations have been performed with the $ab\ initio$ pseudopotential approach based on Density Functional Theory, implemented in the Quantum-Espresso package [12].
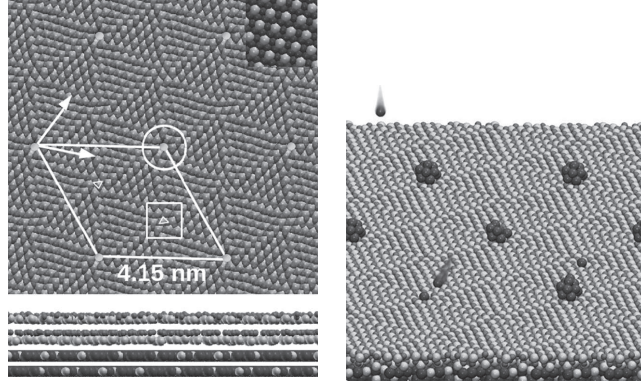
Fig. 1. – Left panel: top (upper) and side view (lower) of the structural model of $Al_2O_3/Ni_3Al(111)$ (underlying $Ni_3Al(111)$ in the inset), with the sketch of the periodically repeated unit cell and the directions of the primitive vectors of the underlying alloy. White circle and square indicate the reduced models used in the simulations around the sites of interest, namely, "hole" and "network" sites, respectively, and shown magnified in fig. 2. Small medium grey balls: O atoms; small light grey: Al; small dark grey: Ni. Right panel: perspective view of a model describing an ordered array of Cu NPs (Cu atoms: large grey balls) anchored at the "holes" of alumina thin film, with impinging and diffusing isolated Cu atoms.

Ultrasoft pseudopotentials and spin unrestricted generalized gradient approximation in the Perdew-Burke-Ernzerhof formulation for the exchange and correlation functional have been used. Other technical details are reported in [7, 13, 14]. For the simulation of supported NPs, it is possible to consider reduced models of the alumina film around the anchoring sites, containing a portion of the oxide film and two layers of the metallic alloy under the oxide, as shown in fig. 1, containing about 130 atoms. The total energy calculations allow to obtain equilibrium geometries, energetics, charge distributions. In particular, the adsorption energy of individual metallic atoms can be calculated subtracting the total energy of the $Al_2O_3/Ni_3Al(111)$ substrate (Subs) and the isolated metallic atom (Me) to that of the entire system (Subs + Me)

$$(1) \qquad E^{Ads} = E_{Subs+Me} - E_{Subs} - E_{Me}.$$

With this definition, the adsorption energy is negative.

The simulations of the first stages of atom-by-atom nucleation of NPs on the alumina film have been performed for Cu and other transition metals (Fe, Co, Ni, Pd, Ag, Au). The investigation of the interaction of CO is limited to Cu NPs. The experiments have been focused, in fact, on Cu, that has been deposited on the alumina template by CVD. Carbon $1s$ core level spectra have been then acquired using *in situ* X-ray photoemission at the SuperESCA beamline of the ELETTRA Synchrotron in Trieste, both i) under exposure of NPs to CO at liquid N_2 temperature, ii) at saturation and iii) upon heating [14].

3. – Metal seeding on $Al_2O_3/Ni_3Al(111)$

In connection with experiments, that have been focused on Cu NPs, we have performed detailed calculations on Cu. With the purpose of understanding the possibility
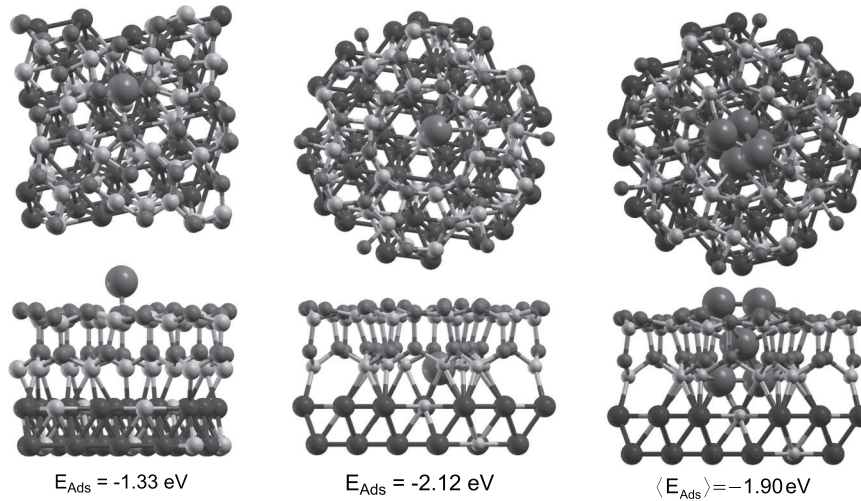
E_{Ads} = -1.33 eV E_{Ads} = -2.12 eV $\langle E_{Ads} \rangle = -1.90$ eV

Fig. 2. – DFT final configurations and adsorption energies of: one Cu atom at the "network" site (left panels), inside the hole of alumina thin film (middle panels), the biggest seed that can be accommodated in the hole, with 6 Cu atoms (right panels). Top/bottom panels are top/side views of the reduced models used for the calculations. Small medium grey balls: O atoms; small light grey: Al; small dark grey: Ni. Large grey: Cu.

of seeding in specific sites, we have studied single Cu ad-atom diffusion on the oxide film. The low diffusion barriers, not exceeding 0.5 eV, indicate that diffusion is effective at room temperature, allowing preferential adsorption in the defect sites (holes) of the "dot" structure with respect to the "network" one, since the predicted adsorption energy is about 0.8 eV stronger (fig. 2, left and middle panels). The metal atom lies at the bottom of the hole, as expected, interacting directly with the underlying Ni_3Al alloy. Atom-by-atom, seeds with up to 6 atoms accommodated in the hole can be formed, offering a stiff anchoring to the support for further nucleation of NPs (fig. 2, right panels), with an average adsorption energy of -1.90 eV.

Beyond Cu, we have investigated the adsorption of other transition metal atoms in the "hole" and "network" sites: Fe, Co, Ni from the fourth period of the Periodic Table, Pd and Ag from the fifth, and Au from the sixth. Figure 3 summarises the results. The adsorption energy varies considerably from one atom to another, and the trend can be rationalized in terms of atomic size and electronic properties (charge distribution, density of states, position of the d-level center) [13]. However, the "hole" is in any case the preferential site. The adsorption in the "network" structure can occur in three different nearby sites, indicated in the model: hollow (H), bridge (B), top (T).

To generate an ordered array of nanoclusters by self-assembly, it is necessary that the metallic atoms deposited through CVD adsorb preferentially only in one of the sites on the surface, generating seeds geometrically dispersed, and that the adsorption energy in that site is strong enough. The most efficient seeding would correspond to the transition metal with a strong adsorption energy in the hole, and a high difference with respect to the sites of the "network" structure. Pd is peculiar, having a strong adsorption energy in the hole (-2.74 eV), more than 1.5 eV stronger than the one in the most attractive "network" site. In comparison, the corresponding values for Cu are -2.12 eV and 0.80 eV.

Not only thermodynamics but also kinetics may play an important role in the nucleation of different metals on the substrate. The calculated surface diffusion barriers for
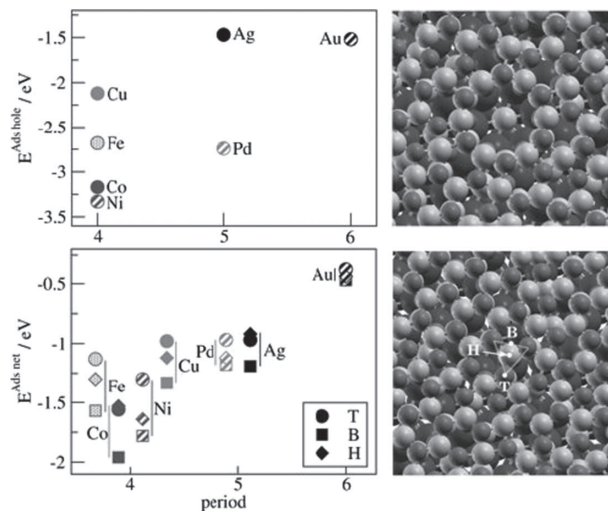
Fig. 3. – Left panels: DFT adsorption energies of several transition metal atoms in the "hole" of the alumina film (upper panel) and in three inequivalent sites (hollow (H), bridge (B), top (T)) close to the three-fold "network" position (lower panel). Right: top view of the corresponding structural models of the alumina film around the adsorption sites. Small medium grey balls: O atoms; small light grey: Al; small dark grey: Ni.

Pd are very low, even lower than those for Cu: this can be explained by the different affinity of the metals towards oxygen. The Pd atoms which attach weakly to the oxide will easily diffuse, and arriving randomly through CVD would find it easy to reach the preferential nucleation sites. Our calculations offer thus a rationale to what has been previously reported in the literature [5, 6, 10]: Pd is indeed one of the best candidates for creating a seed inside the hole and for further proceeding with nucleation of another desired metal.

4. – CO chemistry on supported Cu nanoclusters

Motivated by the peculiar catalytic behaviour of Cu-based surfaces for the CO and CO_2 chemistry [15, 16] we proceeded focusing on Cu self-seeded nanoclusters. Experimentally, different Cu coverage values with respect to the clean Ni_3Al surface have been considered. From the value of the Cu coverage, the average cluster size has been calculated considering that the nucleation, anchoring, and growth of the Cu clusters occurred at the holes of the alumina film: the estimated size of the smallest clusters results to be of about 30 atoms. Due to the huge computational effort that the description of such systems would require in a fully quantum mechanical approach, we limited to smaller clusters, containing up to 15 atoms, 2 of which constitute the anchoring seed. Although smaller, they catch the main peculiarity of the real system, that is the finite size and curvature of the exposed surface.

The interaction of CO with Cu nanoclusters has been then studied comparing simulations with *in situ* X-ray photoemission spectroscopy measurements. We address the reader to ref. [14] for all the details of the experimental results. We only summarize here the main conclusions that can be obtained from the spectra acquired during CO expo-

sure at liquid nitrogen (LN_2) temperature, at saturation, and upon heating, following the evolution of the peaks due to atomic carbon species (carbide) and to the molecular CO adsorbed at the Cu clusters. During the uptake at LN_2 temperature, the CO molecule undergoes dissociation and atomic carbon accumulates at the clusters, at variance with single-crystal surfaces. The evolution of the peaks due to the atomic carbon species upon CO exposure indicates that CO dissociation is promoted by the local CO coverage. Both adsorption and dissociation, in turn, are favoured by increasing the sample temperature and the gas pressure. Concerning the role of the cluster size, a clear size dependence can be observed in the experiments, that have been repeated for cluster size up to 200 atoms, showing that the smaller the cluster, the more reactive it is with respect to CO dissociation.

DFT calculations shed light on the atomic-scale mechanisms governing such processes. On ideal single crystal Cu(111) surfaces, the direct dissociation is highly endothermic, with an unfavored energy balance of about 2 eV. The Boudouard reaction is also endothermic, by about 0.5 eV.

We then considered the CO interactions with Cu nanoclusters. The energetics is shown in fig. 4, together with the models obtained by DFT. Considering the finite size effect and a low CO coverage (left upper panel, with free-standing clusters of 13 Cu atoms), both the direct CO dissociation (central upper part of each panel) and the Boudouard reaction (right part) remain endothermic, although the energy balance is less unfavored (1.38 eV and 0.43 eV the final energy variation for the two reactions). Interestingly, CO coadsorption (central lower part of each panel), that could give rise to the Boudouard reaction through a Langmuir-Hinshelwood mechanism, is much more favoured.

The scenario changes significantly upon increasing the CO coverage, going towards values exceeding that achievable on single crystal surfaces. In the small Cu cluster fully covered by CO molecules (right upper panel), coadsorption is favoured, direct dissociation of CO occurs practically at no cost, and the Boudouard reaction becomes exothermic. The high reactant coverage is indeed the leading factor. Finally, we considered in our simulations also the presence of the support (lower panel): this makes the clusters more malleable and clearly favors the Boudouard process with respect to further adsorption of CO.

5. – Conclusions

We have studied the seeding and nucleation of different transition metal species on the alumina films supported by $Ni_3Al(111)$. By considering the adsorption energies in different adsorption sites, we give a rationale for the experimentally observed different behaviour of metals nucleating on this substrate. For Cu, adsorption inside defective hole sites is clearly preferred. Pd is even more promising to create highly ordered seeds, due to the stronger preference towards the holes and lower diffusion energy barriers, which makes it very easy to diffuse on the oxide surface and reach the preferential nucleation sites.

Motivated by the peculiar catalytic activity of Cu-based surfaces, we have then focused our attention to the interaction of Cu-supported nanoclusters with CO. At variance with single-crystal surfaces, on the Cu clusters reactions involving CO dissociation occur, such as the Boudouard reaction. The latter becomes exothermic and is made possible by the combined contribution of support, finite size effects, and local coverage of the reactant molecules, that in the exposed curved surfaces of nanostructured systems can reach the supramonolayer limit.

+1.38 eV

+0.43 eV

-1.51 eV

Cu_{13}

+0.07 eV

-0.62 eV

-1.05 eV

Cu_{13}

CO coverage

support

+0.31 eV

-0.59 eV
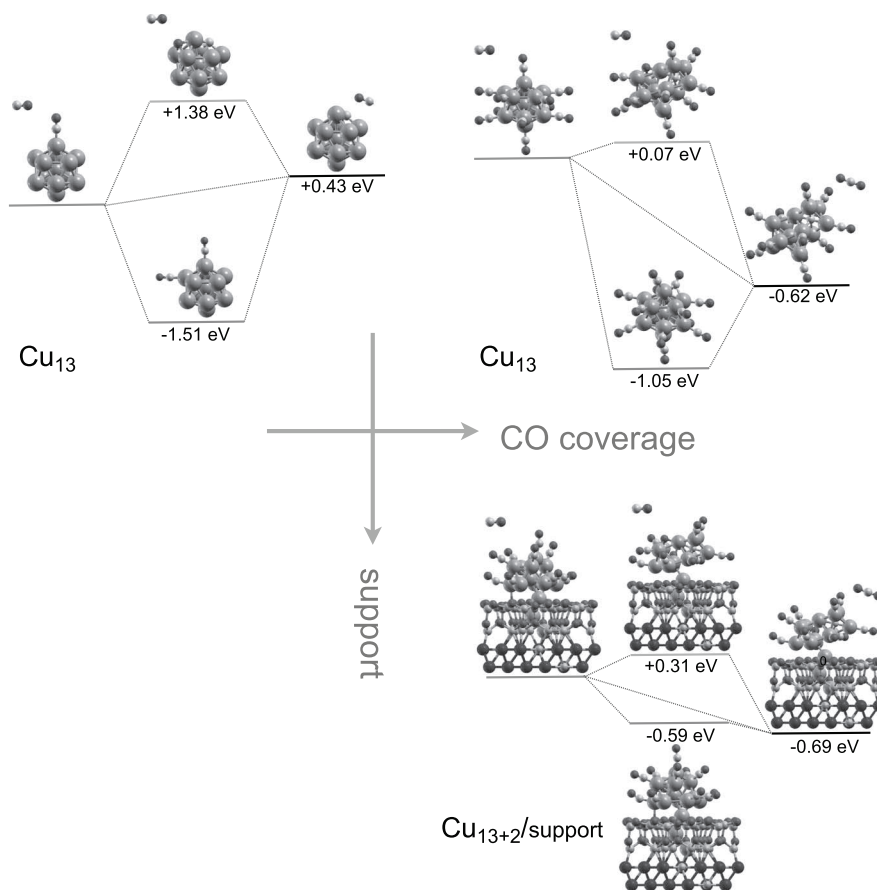
-0.69 eV

Cu_{13+2}/support

Fig. 4. – DFT energetics of CO adsorption, direct dissociation, and Boudouard reaction on a small Cu nanocluster free-standing (upper panels) and supported onto alumina/$Ni_3Al(111)$ (lower panel). Left upper panel is for low CO coverage, whereas the others are for high coverage. Large medium grey balls: Cu; small light grey: C; small dark grey: O. For other elements in the lower panel, see caption of fig. 2.

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