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Cobalt on nickel surfaces and the role of carbide on its stability

S. Stavrić[1][2], V. Chesnyak[1][3], M. Panighel[3], G. Comelli[1][3],
C. Africh[3] and M. Peressi[1](*)

[1] *Dipartimento di Fisica, Università degli Studi di Trieste - Trieste, Italy*
[2] *Vinča Institute of Nuclear Sciences - National Institute of the Republic of Serbia,*
    University of Belgrade - Belgrade, Serbia
[3] *CNR-IOM, Laboratorio TASC - Basovizza, Trieste, Italy*

Summary. — Transition metal atoms are commonly used in catalysis and photo-catalysis, but their potential reactivity reduces with aggregation and alloying. We investigate in particular whether Cobalt adatoms float on Ni surfaces or dissolve into the metal. Density functional theory calculations have been performed in order to evaluate the stability of different Cobalt adsorption configurations on Nickel surfaces, mainly at (100) terraces and steps, and the relevant energy barriers for diffusion on terraces and across steps, segregation and dissolution into the substrate. The simulations have been compared with variable temperature scanning tunneling microscopy and low energy electron diffraction. The results show that the Cobalt adatoms and small aggregates are unstable with respect to the formation of Co-Ni alloys, but the presence of a carbide monolayer on Ni surface improve their stability.

1. – Introduction

Cobalt (Co) is particularly interesting as a potential catalyst and has peculiar magnetic properties. Nickel (Ni) is a widely available and cheap substrate to support Co-based nanocatalysts, but the challenge is to keep thermally stable configurations, preventing mixing and dissolution of the adsorbate into the support.

To this purpose, we investigate and compare the behavior of single adatoms and small Co aggregates on different Ni-based surfaces: bare Ni(100) surface and a carbide (Ni_2C) covered Ni surface, that we obtained with different growth protocols [1].

We report here the main results of a joint theoretical/experimental investigations, that include full spin-polarized density functional theory (DFT) simulations with the Quantum Espresso suite of codes [2] and a DFT-based model and state-of-the-art surface science techniques such as variable temperature scanning tunneling microscopy (STM) and low energy electron diffraction (LEED).

(*) E-mail: `peressi@units.it`

2. – Results

After having prepared different Ni surfaces, whose structure has been characterized by LEED [1], we have evaporated Co at room temperature. On bare surface, the Ni(100) terraces are partially covered by small, randomly distributed bright protrusions about 2 Å high. These structures are assigned to 2D monolayered Co islands (fig. 1, left). On the carbide-covered surface, fewer yet wider islands with a more irregular shape are clearly visible. Such islands, also assigned to Co, are higher than one atomic layer, thus indicating a three dimensional (3D) growth (fig. 1, right). At variance with bare Ni(100) surface, the steps of the carbide-covered substrate always display a jagged shape and often appear to be decorated, likely by Co atoms.

In order to rationalize the observed difference in the Co behaviour on the two surfaces, we performed DFT calculations using the generalized gradient approximation. The systems were modeled using 4×4 slabs (and 6×6 for larger clusters) in a periodically repeated tetragonal unit cell with four Ni layers and using $(3, 3, 1)$ (and $(2, 2, 1)$) Γ-centered k-point grids for Brillouin zone integration. Further details can be found in [1].

We first address our attention to the structure and stability of Co aggregates. We calculate their binding energy (normalized to the number of Co atoms in the cluster) as

$$(1) \qquad E_{\mathrm{bind}} = \frac{1}{n}\left(nE(\mathrm{Co}) + E(\mathrm{S}) - E(\mathrm{Co}_n/\mathrm{S})\right),$$

where n is the number of Co atoms in the cluster, $E(\mathrm{Co})$ is the total energy of a Co atom in the gas phase, $E(\mathrm{S})$ is the total energy of the surface and $E(\mathrm{Co}_n/\mathrm{S})$ is the total energy of the cluster adsorbed on the surface. With this definition, the binding energy is positive if the structures are stable, and higher values indicate higher stability.

Figure 2 shows the calculated binding energy of Co clusters containing up to 26 atoms in their most stable 2D and 3D configurations on bare Ni and carbide-covered surfaces. The most stable configuration for an individual adatom corresponds to the adsorption in the site with the highest coordination on both surfaces. The binding energy per atom increases with the number of Co atoms: already in dimers and trimers a strong Co-Co attractive interaction is evident, in particular on carbide.
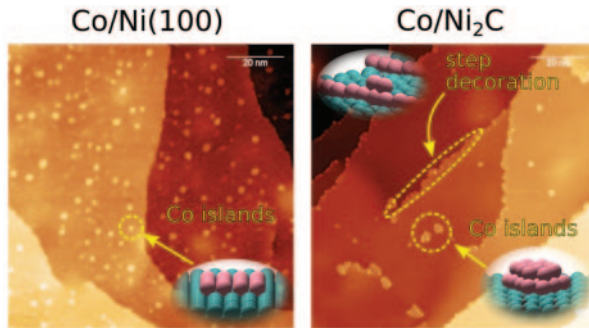

Fig. 1. – Co nanostructures on Ni(100) and Ni$_2$C surfaces. Co forms small, randomly distributed, one-atom high islands on Ni(100) and larger, randomly shaped islands, more than one-atom high, on Ni$_2$C. Besides, Ni$_2$C terraces show jagged, Co-decorated step edges. Atomistic models of the different Co structures are shown in the insets.
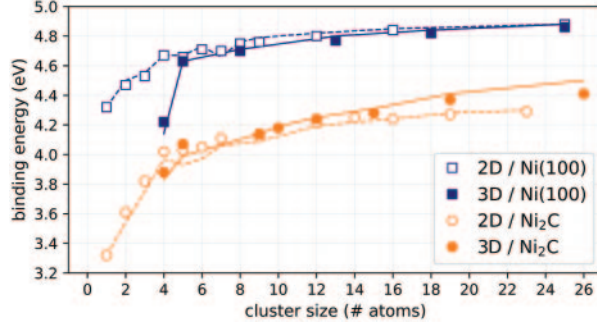
Fig. 2. – Binding energy per atom of Co clusters on Ni(100) and carbide. Symbols (squares and hexagons for Ni(100) and carbide, respectively) represent the results from full DFT calculations; lines from the model. Open/solid symbols and dashed/solid lines denote 2D/3D structures.

On Ni(100) the preference is always for 2D structures, in particular for small clusters, which are the first steps of the growth process. Since the barrier for one atom to climb from the first to the second layer is very high (about 2.5 eV), we argue that, although the 2D and 3D structures become almost degenerate for large clusters, kinetic arguments are against 3D growth. This perfectly agrees with the STM observations, which never show 2-layer-high Co structures on Ni(100). At variance, Co atoms prefer to arrange into 3D clusters on Ni_2C. Furthermore, climbing from a first to a second layer in this case has a barrier which is half the value on Ni(100).

The difference in the preferred cluster growth mode on the two surfaces can be quantitatively explained by a simple model. We limit to 2-layer structures, as suggested by experimental observations. The model takes into account the number of Co atoms in the first/second layer and different energy terms that can be associated to vertical or lateral interatomic interactions, extracted from selected DFT calculations. The binding energy per atom of a Co cluster with n_1 atoms in contact with the Nickel surface and n_2 atoms in the second adlayer can be approximately split into different contributions:

$$(2) \qquad \widetilde{E}_{\text{bind}} = \frac{1}{n}\left(n_1 E_1 + n_2 E_2 + n_b E_b\right), \quad n = n_1 + n_2,$$

Fig. 3. – Sketch of three different steps possibly occurring in the process of Co aggregation on Ni(100) (left) and Ni_2C (right): 1) adsorption of an individual Co adatom (energy gain: $-E_1$); 2) addition of a Co adatom to the first layer of an existing island (with a further energy gain of $-E_b$ for each Co-Co bond in the first layer); 3) addition of a Co adatom in the second layer (with a further energy gain of $-E_2$ for each Co-Co bond between the two layers).

where E_1 (E_2) is the energy associated with the bond that each Co atom in the first (second) adlayer forms vertically with the underlying Ni (Co) atoms; n_b (E_b) is the number (energy) of first-neighboring lateral Co-Co interaction. The values of the energy terms E_1, E_2, E_b, derived from full DFT calculations on a few small clusters and a schematic picture of their meaning are shown in fig. 3. Equation (2) allows the estimation of the binding energy of one or two atomic layers clusters of any size.

DFT calculations also allow understanding the different appearance of the edges. In fig. 1, the Ni steps appear to be sharp and uniform, whereas the Ni_2C edges are irregular and covered by Co. DFT calculations show that a single Co adatom prefers to bind at the foot of the step in both cases. However, the diffusion barrier on the terraces is different: 0.8 eV on Ni(100) and nearly half (0.4 eV) on Ni_2C. Therefore, a Co atom can easily diffuse on Ni_2C terraces. When this atom reaches a step edge which is already Co-decorated, it stays there, because the barrier to jump down is high, 1 eV.

Finally, we examine the thermal stability of the Co clusters on both substrates increasing the temperature. Co islands are visible at 200 °C on Ni(100), but some of them disappear after few minutes; when temperature increases to 250 °C, only a few small islands are still there. Conversely, at 200 °C some islands and step decorations are clearly visible for a longer time on Ni_2C; at 300 °C, the step decorations disappear but the islands are still visible. In summary, the dissolution process of Co occurs sooner or later, but it is slower on carbide and occurs at a higher temperature than on the clean Ni(100) surface. This can also be rationalized by DFT, although calculations are performed at 0 Kelvin: DFT shows that Co prefer to occupy subsurface sites in both cases, but the barrier for its dissolution from surface to subsurface is higher on carbide than on Ni(100) surface.

3. – Conclusions

In summary, the present investigation on the stability of Co adatoms and small aggregates on Ni surfaces shows that Co adatoms and small aggregates are unstable with respect to the formation of Co-Ni alloys on bare Ni(100) surface, whereas carbide acts as a protective layer against Co dissolution into bulk, *i.e.*, enhances the stability of Co on the surface. This is essential to preserve the potential reactivity of the transition metals adatoms and to exploit their catalytic properties.

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REFERENCES

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