

# Ab Initio simulation of carbon clustering on Ni(111) surface: the bonding mechanism between carbon and nickel

S. Meloni

CASPUR - Consorzio per le Applicazione del Supercalcolo  
per Università e Ricerca  
via dei Tizii, 6b, 00185, Roma, Italy

## 1 Introduction

Transition metal catalysts are used in a great number of industrially important reactions, such as methanation, which consists in the dissociation of CO and subsequent formation of methane [1,2]. During these processes, carbon absorption on the nickel surface occurs. There are two main carbon phases identified. The first one is the active carbon phase leading to hydrocarbon product formation, named "carbide" phase. In this phase reactive carbon atoms are distributed more or less uniformly over the transition metal surface. This implies that in this phase the coverage can not be too high since a high packing will induce clustering and therefore reduce reactivity. The second phase is the inactive carbon phase leading to catalyst deactivation, named "graphitic" phase. In this phase a graphite monolayer bonded to the surface is formed and the catalyst is rendered inactive.

Due to its technological and fundamental importance, this problem has attracted a lot of attention recently, both in experimental and theoretical studies [3–11].

In our previous work [12], we studied the poisoning of nickel (111) surface due to carbon. Performing ab-initio simulations, within the framework of Free Energy Functional approximation to the Density Functional Theory, as proposed by Alavi et al. [13,14], we computed the surface energy of the nickel (111) surface as a function of carbon coverage  $\theta$ , going from 0 (empty surface) to 1 (carbon monolayer). From the dependence of that surface energy as a function of coverage we deduced that only an empty surface or a fully covered surface with graphene are stable thermodynamics states of the nickel surface in contact with carbon vapor at constant pressure. We have also identified the lowest surface energy configurations of the nickel/carbon surface at different coverages.

In the present work, we focus on describing the electronic structure of carbon compounds adsorbed on the nickel (111) surface in order to understand the nature of bonding between carbon and nickel (111). To this aim, we make use of effective molecular orbitals [15] (EMOs). These orbitals are a linear combination of maximally localized Wannier orbitals [15,16,18–21] such that they are still localized either on the carbon subsystem or on the nickel slab.

During the visit supported by SimBioMa, we developed an interpretative scheme of our ab-initio calculations. This scheme is reported in the next session.

## 2 Interpretative scheme of the $C_n/Ni$ bonding

The electronic structure of carbon systems adsorbed on nickel was studied with the help of maximally localized Wannier orbitals. These orbitals are defined as a unitary transformation of the occupied Kohn-Sham orbitals:

$$w_i = \sum_n V_{in} \psi_n, \quad (1)$$

where  $V_{in}$  elements of the unitary matrix  $V$  are such that they minimize a spread functional:

$$\Omega(V) = \sum_i (\langle w_i | \mathbf{r}^2 | w_i \rangle - \langle w_i | \mathbf{r} | w_i \rangle^2). \quad (2)$$

This functional definition, correct for isolated systems, can not be used as such for periodic systems since the position operator  $\mathbf{r}$  is ill-defined. Several authors [15–21] have extended the functional of eq. (2) to the case of periodic systems. In particular, in this work, we use the spread functional introduced by Resta [17] and generalized by Berghold et al. [21], which is proper for the calculation of maximally localized Wannier orbitals at the  $\Gamma$ -point.

The usual approach for an insulating system is to consider a rotation of the occupied orbitals to determine the maximally localized orbitals. Here, for a metal and employing a free energy density functional theory, a different choice of orbital space has to be made since the occupation number varies smoothly across the Fermi energy. Two recent approaches have been proposed to construct an orbital space to determine Wannier orbitals for entangled bands [18] or for partially occupied Wannier orbitals [19]. Here, we take a different approach. We simply specify *a priori* the number  $N$  of orbitals to be included in the functional space of eq. (1).  $N$  is chosen such that the energy of the last orbital is well above the Fermi energy and such that a significant gap is found above the  $N^{\text{th}}$  orbital. This way, all the (partly) occupied orbitals are taken into account in the transformation.

In this work, we inspect how Kohn-Sham orbitals of the isolated carbon and nickel systems are modified under deposition of carbon on nickel surface. In order to do so, we propose to construct Effective Molecular Orbitals (EMOs) for the composite system that would have the two properties of being localized on each subsystems, carbon and nickel, and converge to the Kohn-Sham orbitals for infinite separation of carbon and nickel. We consider a possible definition of EMO's, following the procedure by Hunt et al [15], as being the eigenfunctions of an effective hamiltonian defined for each subsystem by the projection of the true Kohn-Sham hamiltonian on a suitable set  $S$  of maximally localized Wannier orbitals:

$$\hat{H}_{eff}^S = \sum_{ij \in S} |w_i\rangle \langle w_i | \hat{H} | w_j \rangle \langle w_j| \quad (3)$$

To this aim, we have grouped the maximally localized Wannier orbitals in two sets of orbitals, assigned to nickel or to carbon depending on the distance from the Wannier center to the carbon or nickel atoms. The localization of the Wannier orbitals was always found sufficient to unambiguously assign the localized orbitals either to nickel or to carbon parts of the system. For infinitely separated systems, the so-constructed EMOs converge towards the Kohn-Sham orbitals of the isolated sub-systems. This can easily be seen starting from the restriction,  $\hat{H}_N$ , of the total Hamiltonian to the orbital space of the  $N$  lowest Kohn-Sham orbitals used for the construction of the MLWF:

$$\hat{H}_N = \sum_{n=1}^N |\psi_n\rangle \epsilon_n \langle \psi_n|, \quad (4)$$

where  $\epsilon_n$  are the eigenvalues associated to the Kohn-Sham orbitals  $\psi_n$ . Introducing the projectors on the MLWF orbital spaces associated to carbon and nickel,  $\hat{P}_C = \sum_{i \in C} |w_i\rangle \langle w_i|$ ,  $\hat{P}_{Ni} = \sum_{i \in Ni} |w_i\rangle \langle w_i|$ , this

Hamiltonian can be recasted as:

$$\begin{aligned}\hat{H}_N &= \hat{P}_C \hat{H}_N \hat{P}_C + \hat{P}_{Ni} \hat{H}_N \hat{P}_{Ni} + \left( \hat{P}_C \hat{H}_N \hat{P}_{Ni} + \hat{P}_{Ni} \hat{H}_N \hat{P}_C \right) \\ &= \hat{H}_{eff}^C + \hat{H}_{eff}^{Ni} + \hat{H}_{mix}\end{aligned}\quad (5)$$

For infinite separation between carbon and nickel, the mixing term  $\hat{H}_{mix}$  tends to zero (no overlap between the MLWF orbitals of one subsystem with those of the other subsystem) and the effective Kohn-Sham hamiltonians associated to each subsystem converge to the isolated systems Kohn-Sham hamiltonians (apart known problems that sometimes occur with DFT). In the limit of infinitely separated systems, the EMOs will then converge to the true Kohn-Sham orbitals of the two sub-systems.

We therefore intend to compare the Kohn-Sham orbitals of the isolated systems and the corresponding EMO's of the carbon compound on the Nickel surface. This analysis may consists both in the comparison of the "shape" of the Kohn-Sham orbitals of the isolated system with the EMO's of the carbon compound on Ni(111) and the comparison of the eigenvalues of the isolated carbon compound with the one associated to the EMO's for the effective hamiltonian introduced above. These differences account for the effect of the "field" of the nickel and the electron transfer from the metal surface to the carbon compound. This latter can be measured by calculating the occupation number of the EMO's (the occupation number can be fractional in our case).

A second step in the analysis consists in assuming that the actual Kohn-Sham orbitals are a first order perturbation of EMOs. Within this hypothesis, the Kohn-Sham orbital  $\psi_n$  are equal to

$$\psi_n = \phi_l + \sum_{l \in S'} \frac{\langle \phi_k | \hat{H}_{mix} | \phi_l \rangle}{|\alpha_l - \alpha_k|} \phi_k \quad (6)$$

where  $\phi_k$  and  $\phi_l$  are the EMOs,  $\alpha$  are the eigenvalues of the effective Hamiltonians  $\hat{H}_{eff}^C$  and  $\hat{H}^{Ni}$  associated to the EMOs, and the sum runs over the EMOs belonging to the set  $S'$  complementary to the set  $S$  to which  $\phi_l$  belong to (by construction the matrix elements  $\langle \phi_k | \hat{H}_{mix} | \phi_l \rangle = 0$  for  $k, l \in S$ ). If  $\hat{H}_{mix}$  is a small perturbation eq. 7 is valid. On the other hand, if  $\hat{H}_{mix}$  is not just a small perturbation the quantity  $\Delta H_k = \sum_{l \in S'} |\langle \phi_k | \hat{H}_{mix} | \phi_l \rangle| / |\alpha_l - \alpha_k|$  is a measure of the order of mixing of orbitals belonging to carbon compounds and nickel. This measure is important as the amount of the mixing is an indication of the order of covalent bonding and/or the formation of "surface states" upon deposition. For performing this type of analysis we use the following simplified formula

$$\Delta H_k = \frac{1}{|\bar{\alpha} - \alpha_k|} \sum_{l \in S'} |\langle \phi_k | \hat{H}_{mix} | \phi_l \rangle| \quad (7)$$

where  $\bar{\alpha}$  is the average of the  $\alpha$ s associated to the effective Hamiltonian  $\hat{H}^{Ni}$ .

For concluding this report, here I present the results obtained applying this scheme to the deposition of a carbon ad-atom on the Ni(111) surface:

Data reported in table 1 shows that the interaction of the carbon ad-atom with the surface has two effects: i) stabilization of (some of) the carbon orbitals by  $\sim 2.3$  eV, ii) brake of the symmetry among  $p$  orbitals. The overall effect of this interaction is a net electron transfer of  $\sim 1.8$  electrons from the Ni(111) to the carbon atom. On top of this there is the effect of the mixing of the carbon and nickel EMOs as measured by the  $\Delta H_k$  (see Table 1 and Fig. 1). From these data we deduce that the interaction between the  $s$  state of the carbon atom and the surface is negligible (see the isolated bar at about  $-11$  eV in Fig. 1 top-left panel). On the other hand,  $p_y$ ,  $p_z$  and especially  $p_x$  have a strong mixing with the Ni EMOs, indicating the possible formation of covalent bonds.

orbital	energy C	energy C/Ni	oc. C	oc. C/Ni	$\Delta H_k$	character
1	-8.3853	-10.5898	2.000	1.955	0.27	$s$
2	0.0597	-0.9962	0.667	1.045	6.91	$p_x$
3	0.0597	-2.7496	0.667	1.452	1.83	$p_y$
4	0.0598	-2.2510	0.667	1.388	2.57	$p_z$

Table 1: Energies (with respect to the chemical potential), occupation numbers and  $\Delta H_k$  values for an isolated carbon atom, in vacuum or adsorbed on nickel

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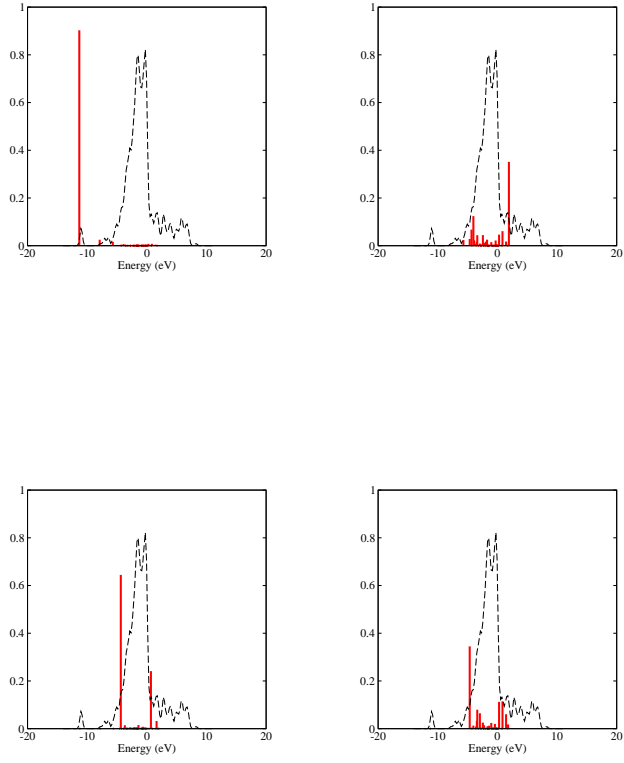


Figure 1: Density of states of a carbon ad-atom upon Ni(111) superimposed to the density of states of the C/Ni(111) system. Top-left  $s$  EMO, top-right  $p_x$ , bottom-left  $p_y$ , bottom-right  $p_z$ . The orientation of the axis is such that the surface is along  $x$