

# Reactivity of a Pt(100) cluster modified by adsorption of a Nickel tetramer

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**Abstract.** The aim of this paper is to report a study of the reactivity of Pt(100) cluster and the same system modified by a nickel tetramer towards the atomic hydrogen adsorption. This study was carried out in the framework of density functional theory which provides global and local indexes that can be used to characterize the reactivity. The analyzed reactivity descriptors were: chemical potential, chemical hardness, electrophilicity index and Fukui function. The results showed that the global reactivity descriptor predicts that the platinum cluster modified by nickel is more reactive than the pure platinum cluster and that the local Fukui function provides information about the most susceptible site to electrophilic attack in platinum cluster.

## 1. Introduction

There is a strong current interest in the study of supported metal nanoclusters, not only from a fundamental point of view but also because of their technological relevance in, e.g., heterogeneous catalysis or the design of nanoscale magnetic storage devices. Systems with reduced dimensions can exhibit surprising properties [1].

The increase in catalytic properties resulting from the formation of intermetallic compounds is attributed to the alteration of the electronic structure and physicochemical properties, such as work function and density of states at the Fermi level [2].

The system Pt/Ni has been widely studied in its various forms: Alloy surface [3], pseudomorphic overlayer [4] and supported nanoparticles [5]. Recent studies have revealed that the Pt-Ni alloy surface presents a considerable increase in the catalytic activity versus Pt pure compared to the reaction of oxygen reduction [6] and Ni-Pt nanoparticles which are more reactive compared to the oxidation of methanol on the surface of Pt(100) surface [7]. It is therefore of great interest to know the microscopic mechanisms responsible for the modification of the reactivity in this bimetallic system since this knowledge will allow the design of catalysts composition and specific structures.

The Density Functional Theory (DFT) has provided the basis for rigorous mathematical definitions of reactivity descriptors like chemical potential, electronegativity, chemical hardness, softness, etc., [8].

All of these are well established global indicators in chemical reactivity studies and are going to be used in this paper to characterize the reactivity of Pt(100)<sub>n</sub> cluster and Pt(100)<sub>n</sub>Ni<sub>m</sub> (n=25, m=4) toward the adsorption hydrogen atom.

Also local indicators have been introduced in the theory to explain the reactivity or selectivity at a particular site of the system. In this work, we adopted the Fukui function to analyze the reactivity of the surfaces against a hydrogen atom.

## 2. Theoretical background

In DFT, the chemical potential and hardness for the N-electrons system with total energy E and external potential v(r) are defined as the first and second derivatives of the energy with respect to N [8-11]:

$$\mu = \left( \frac{\partial E}{\partial N} \right)_{v(r)} = -\chi \quad (1)$$

and

$$\eta = \frac{1}{2} \left( \frac{\partial^2 E}{\partial N^2} \right)_{v(r)} = \frac{1}{2} \left( \frac{\partial \mu}{\partial N} \right)_{v(r)} \quad (2)$$

In numerical applications,  $\mu$  and  $\eta$  are calculated through the following approximate version of Eqs. (1) and (2), based upon the finite difference approximation and the Koopmans theorems [8],

$$\mu \approx -\frac{1}{2}(IP + EA) = \frac{1}{2}(\varepsilon_L + \varepsilon_H) \quad (3)$$

and

$$\eta \approx -\frac{1}{2}(IP - EA) = \frac{1}{2}(\varepsilon_L - \varepsilon_H) \quad (4)$$

IP is the ionization potential, EA is the electron affinity,  $\varepsilon_H$  and  $\varepsilon_L$  are the energies of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), respectively. The electrofelicity index is defined as [11]:

$$\omega = \frac{\mu^2}{2\eta} \quad (5)$$

This quantity is a measure of the propensity of systems to acquire electronic charge from the surroundings. Considering clusters or metallic surfaces as binding environments,  $\omega$  can be useful for analyzing the interaction with small molecules.

The condensed Fukui functions are denoted as [10]:

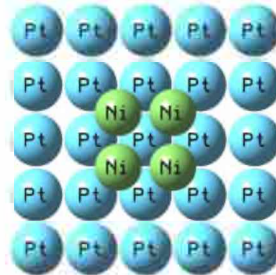
$$\begin{aligned} f_k^+ &= q_k(N+1) - q_k(N) \\ f_k^- &= q_k(N) - q_k(N-1) \end{aligned} \quad (6)$$

where  $q_k(M)$  is the atomic electron population at atom k for either the neutral system (M=N), the cation (M=N-1), or the anion (M=N+1).

## 3. Computational methods

Density functional theory (DFT) as implemented in Gaussian03 [12] has been used for all the calculations. The hybrid B3LYP density functional method was used, which includes Becke's 3-parameter nonlocal-exchange functional [13] with the correlation functional of Lee et al [14]. The effective-core-potential LANL2DZ [15] is used for the atoms of Ni and Pt and the bases 6-31G\*\* for hydrogen atom.

The Pt surfaces with (100) crystalline plane were modeled using Pt(100)<sub>25</sub> clusters and Ni nanoparticles was simulated by a nickel tetramer, Ni<sub>4</sub>, Figure 1. Since the reactivity of the surface is evaluated in terms of global and local indices based on well localized processes of charge transfer between adsorbate-substrate the use of an atomic bilayer was not considered.



**Figure 1.** Pt<sub>n</sub>Ni<sub>m</sub> (n=25, m=4) system

In all calculations the nearest neighbor Pt-Pt distance was fixed at the experimental value [16] of 0.277 nm for platinum. The optimization of the geometry of the Ni ad-atoms was carried out maintaining the geometry of the substrate fixed. The effects of relaxation of the substrate atoms were not considered.

The interaction of the hydrogen atom on Pt (100)<sub>n</sub> and Pt (100)<sub>n</sub>Ni<sub>m</sub> surfaces was optimized in different adsorption sites: on top, bridge and hollow. At each site the H-surface distance was optimized, while all other parameters of these systems were kept frozen. In all cases, harmonic frequency analysis was performed to verify that the optimized structures are local minima.

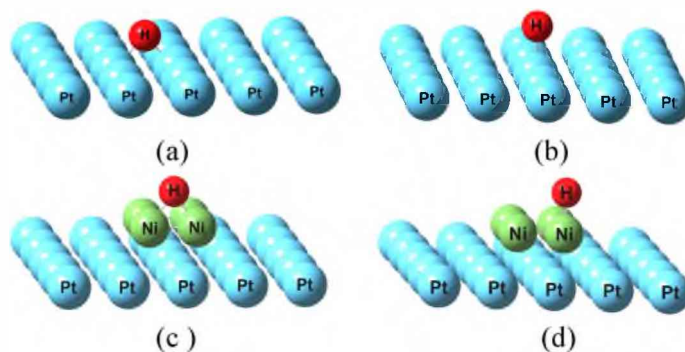
The binding energy of hydrogen atom to the M-H systems (M= P(100)<sub>n</sub>, and Pt(100)<sub>n</sub>Ni<sub>m</sub>) was calculated as:

$$E_{ad} = E_{M-H} - E_M - E_H \quad (7)$$

Where,  $E_{M-H}$  is the energy of hydrogen adsorbed on M system,  $E_M$  energy from the M system and  $E_H$  is the energy of hydrogen to an infinite distance from the surface, respectively.

#### 4. Results

Table 1 shows the values of the global reactivity descriptors -chemical potential ( $\mu$ ), chemical hardness ( $\eta$ ) and electrofilicity index ( $\omega$ )- for the pure and modified surfaces, Pt<sub>n</sub> and Pt<sub>n</sub>Ni<sub>m</sub>, respectively, and the binding energy ( $E_{ad}$ ) of hydrogen atom on Pt<sub>n</sub>H and modified surface, Pt<sub>n</sub>Ni<sub>m</sub>H. The adsorption site of hydrogen atom is indicated as T (on top) and B (bridge), Figure 2. Not found adsorption on the Hollow site.



**Figure 2.** Hydrogen adsorption site (a) Pt<sub>n</sub>H(B), (b) Pt<sub>n</sub>H(T), (c) Pt<sub>n</sub>Ni<sub>m</sub> H(B), (d) Pt<sub>n</sub>Ni<sub>m</sub> H(T)

The reactivity of global indicators is an intrinsic electronic property of the system and indicates their availability for a chemical change that may occur. The chemical potential measures the escaping

tendency of electrons from the equilibrium systems then as  $\mu$  becomes more negative, it is more difficult to lose an electron but easier to gain one.

The chemical hardness can be seen as the strength of a system to charge transfer; therefore it characterizes the stability of the systems under study. The electrophilicity index is a measure of stabilization energy of the system when it is saturated with electrons which come from the external environment, i.e., it measures the tendency of a system to capture electrons.

The chemical potential, the negative of the absolute electronegativity, of the hydrogen atom is  $-7.20$  eV and the chemical potential of  $Pt_n$  and  $Pt_nNi_m$  systems are  $-6.03$  eV and  $-5.92$  eV, respectively (Table 1). Therefore it can be expected that  $Pt_n$  and  $Pt_nNi_m$  systems act as a donor system and the donor Fukui function  $f_k^-$  should indicate the reactivity of different regions of  $Pt_n$  cluster.

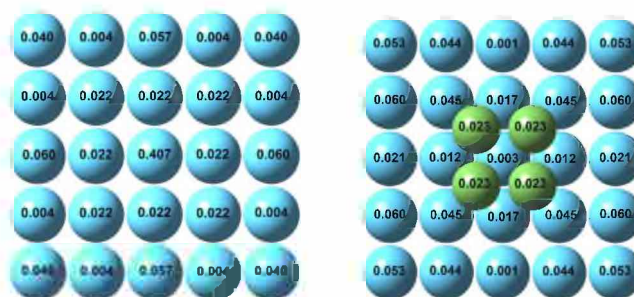
The  $Pt_n$  system had a greater value of chemical hardness,  $0.56$  eV, than the  $Pt_nNi_m$ ,  $0.46$  eV, hence the latter system is more reactive or softer. The hydrogen adsorption stabilizes  $Pt_n$  systems, being  $Pt_nH(T)$  more stable than  $Pt_nH(B)$  with a chemical hardness value equal to  $0.61$  eV and  $0.59$  eV, respectively. The same trend is observed for the modified surface but in this case the  $Pt_nNi_mH(B)$  is more stable than  $Pt_nNi_mH(T)$  with a chemical hardness value equal to  $0.55$  eV and  $0.49$  eV, respectively.

The values of the electrophilicity index confirm the tendency of the system, noting that the lower values of  $\omega$  are for  $Pt_nH(T)$  and  $Pt_nNi_mH(B)$ .

An analysis of the binding energy of hydrogen atom in different sites covering the surface under study confirms that site energetically favorable for  $Pt_n$  cluster is on top and for  $Pt_nNi_m$  is on bridge.

**Table 1.** Global reactivity descriptors, chemical potential ( $\mu$ ), chemical hardness ( $\eta$ ), electrophilicity index ( $\omega$ ) and binding energy ( $E_{ad}$ ) for the systems:  $Pt_n$ ,  $Pt_nNi_m$ ,  $Pt_nH$  and  $Pt_nNi_mH$  ( $n = 25$ ,  $m = 4$ ).

| System         | $\mu$<br>(eV) | $\eta$<br>(eV) | $\omega$<br>(eV) | $E_{ad}$<br>(eV) |
|----------------|---------------|----------------|------------------|------------------|
| $Pt_n$         | -6.03         | 0.56           | 32.41            | -                |
| $Pt_nNi_m$     | -5.95         | 0.46           | 37.93            | -                |
| $Pt_nH(T)$     | -6.02         | 0.61           | 29.70            | -4.64            |
| $Pt_nH(B)$     | -5.93         | 0.59           | 29.80            | -4.45            |
| $Pt_nNi_mH(T)$ | -5.92         | 0.49           | 37.76            | -4.53            |
| $Pt_nNi_mH(B)$ | -5.84         | 0.55           | 31.00            | -6.56            |



**Figure 3.** Fukui function ( $f_k^-$ ) of  $Pt_n$  and  $Pt_nNi_m$  systems.

The Fukui function ( $f_k^-$ ) allows identifying the most active sites in the surface. The greater reactivity of cluster  $Pt(100)_{25}$  is located in the center with maximum value of Fukui function equal to  $0.407$ , Figure 3. This site is the most susceptible to electrophilic attack and this result is in agreement with the previous one for hydrogen adsorption on platinum cluster,  $Pt_nH(T)$ . Reactivity observed in the edge of the platinum cluster atoms can be considered artificial because the border atoms have unsaturated

valences which can cause additional reactivity. The modified surface  $Pt_n Ni_m$  presents the greater reactivity on Ni tetramer with the same value of Fukui function for each Ni atom. The four Ni atom have obviously the same probability to be attacked by electrophilic species, therefore in this case they do not provide the adsorption hydrogen site.

Future studies using larger cluster and effects of relaxation between adsorbate-substrate will allow us to make up a further analysis on the impact of the localized Fukui function to predict energetically favorable adsorption sites.

## 5. Conclusions

The study of the reactivity of Pt(100) cluster and of the same system modified by a nickel tetramer towards the atomic hydrogen using the global and local reactivity descriptors, allows us to arrive at the following conclusions:

-The global reactivity descriptors, chemical potential, chemical hardness and electrophilicity index confirm that the Pt cluster modified by nickel tetramer is more reactive than the pure Pt cluster.

-The local reactivity descriptor, Fukui function ( $f_k^-$ ), predicts that the greater reactivity of pure Pt cluster is located in the central atom and for  $Pt_n Ni_m$  surfaces in the Ni tetramer.

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