



Geometries, Stability, Magnetic Behavior and Electronic Properties of Small Pt_xSn_y ($x + y \leq 5$) Atomic Clusters

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Abstract: The nanoalloying process has allowed us to the possibility of creating new nanomaterials with new properties and new functionalities, one of the most studied nanoalloys both experimentally and theoretically is PtSn. We report the results of our calculations which were carried out to study the equilibrium structures, stability, magnetism and catalytic activity of small free Pt_xSn_y clusters with $x + y \leq 5$, the study was done in the scheme of density functional theory as implemented in SIESTA code in the pseudopotential approach. Our results show that the global minimum structures prefer geometries with high coordination for the atoms, the nanoalloys rich in Sn atoms present a large average bond length and this study reveals a favorable mixing of Pt and Sn atoms, the clusters considered here leaves at least one Pt atom available for chemical reactions; in this regime we found magnetic only in 4 clusters with a ferromagnetic-like order into the nanoalloys. The value of the binding energy per atom increases as the number of Sn atoms decreases in the clusters, the reactivity of the PtSn nanoalloys was studied considering the electron affinity, the ionization potential and the chemical hardness, we found that some clusters with 5 atoms present the lowest value in the chemical hardness making them favorable as catalysts.

Keywords: DFT Calculations, Vertical Electronic Properties, Magnetic Behavior, Reactivity

1. Introduction

The systems at nanometric level have been the object of intense study, in particular the so-called atomic clusters, this is due to their physical and chemical properties depend of the number of atoms in the cluster, therefore their physical and chemical properties can be different in the bulk regime or, more interesting these systems present new physical and chemical properties so make them favorable in technological applications, as in the development of new catalysts, or even in bio-medical applications such as Ag and Au nanoparticles that have plasmon surface in the visible spectrum and this is favorable in the development of biosensors [1].

The development of new techniques of synthesis and production of nano-materials has allowed to synthesize a new type of atomic clusters, those whose constituents are two atoms of different chemical species, known as bimetallic

clusters (BMC) or binary nanoalloys. At nanometric level, the nano-alloying process is under construction and the scientific community is generating data equivalent to the bulk regime, this one of the reasons why BMC have attracted the attention of the scientific community, besides the physical and chemical properties depend not only on the size of the cluster but also on the chemical order into the cluster.

At the nanometer size regime, the study of nanoalloys has become an interesting field of research mainly to the interaction between two chemical elements that leads to changes in the physical and chemical properties in the BMC, for example in the catalytic properties or electronic properties and a more interesting fact, the change in the properties when the chemical order changes in the nanoparticle; but several difficulties have stood in the way of the desired progress in the nanoalloying field, one of them is the difference in the atomic radii, because this difference determines the

conceivable arrangements of the atoms in the BMC, with this, the relative positions of the constituent atoms with a given stoichiometry increase the number of possible geometries for the BMC.

In catalysis, one of the chemical elements most used is platinum because presents a high catalytic activity, but is possible to improve the catalytic properties, binary alloys based on platinum such as Pt-Co [2, 3], Pt-Ni [2], Pt-Pd [4] and Pt-Sn [5-8] have been studied experimentally and the results show that these alloys present a better catalytic activity. Several groups have incorporated Sn on Pt and they have studied the changes on electronic properties of platinum, the studies reveal an enhancement in the electro-catalytic activity [6].

In particular, electrocatalysts PtSn alloys on Carbon present a better activity for methanol and ethanol oxidation than the commercial PtSn/C [7]; the authors show that this oxidation activity is much better when the Pt: Sn alloys were prepared with atomic ratios 3:1.

At the nanometer size regime both pure Pt clusters and pure Sn clusters have been widely studied theoretically, for example, Sebetci and Güvenc studied the energetics and the global minimum structures of small Pt_x ($x = 2-21$) clusters by using the embedded atom model [9]; Yuan et al studied the magnetic properties in Pt clusters in the DFT scheme as implemented in VASP code [10], and Kumar and Kawazoe studied the evolution and electronic structure of Pt clusters [11], this study was done by using VASP code.

Sn free atomic clusters have been studied theoretically into the DFT scheme, Yang and Li [14] studied the thermal stability and the structural evolution of Sn_x ($x = 2-20$); Majumder and co-workers made a study of the atomic and electronic structures with different exchange-correlation functionals [15], and the structure and electric properties of Sn_x ($x = 6-20$) clusters were considered by Schäfer and co-workers [16, 17].

In this work, we studied stability and the vertical electronic properties such as electron affinity, ionization potential and chemical hardness as an index of catalytic activity of very small Pt_xSn_y ($x + y \leq 5$) nano-alloys.

Our work is presented as follows: in the next section the computational method used here is briefly recalled, as well as the values of the parameters involved in the calculation and belong to the SIESTA program. Our Results for global minimum structures of the nano-alloys considered here are presented and discussed in section 3; finally, section 4 summarizes the main conclusions our work.

2. Computational Details

Our work was performed in the DFT scheme by using the free code SIESTA [18] which solves the Kohn-Sham equations in the pseudopotential approach. We employed non-local conserving Troullier-Martins [19] pseudopotential that is factorized in the Kleinman-Bilander [20] form. For the exchange-correlation potential we used the Perdew-Burke-Ernzerhof form of the generalized gradient approximation (GGA) [21]. The pseudo-potentials are considered using the

natural electronic configuration, for Sn atom $5s^25p^2$. For Pt atom we have used the atomic configuration $5d^96s^1$.

The valence states were described using a double- ζ basis set. In the calculations, the clusters were placed in a cubic supercell of a side size of 20 Å. This cell is large enough to warranty that the interactions between the cluster and its replicas in neighboring cells is negligible and we considered only the Γ point when integrating over the Brillouin zone as usual in finite systems.

The energy cutoff used to define the real space grid for the numerical calculations involving the electron density was 250 Ry. Furthermore, by using a conjugate gradient method, a large number of spin states were also considered for every cluster structure with the aim of finding its corresponding lowest energy spin isomer, besides we considered parallel arrangements of local magnetic moments as well as antiparallel arrangements between them. All the structures were fully relaxed without geometry or spin constraints until the forces were smaller than 0.003 eV/Å.

We must mention that in our calculations we have considered several starting geometries, planar geometries and three dimensional geometries, and in all these cases the work is more laborious since we have to take into account all possible positions that atoms can take in the structure; and for each of these geometries we have allowed them to relax for *the two spin configurations*, i.e., parallel arrangements and anti-parallel arrangements; besides we have tested different spin isomers in all cases to be sure that the ground state was obtained. All this because the electronic properties are very sensitive to the geometry and the chemical order in the nanoparticle.

3. Results for Pure Clusters and Nanoalloys

To guarantee the validity of our study with the approaches considered here, in table 1 we present the results for the dimers involved in this study; we can notice that the pure dimers present magnetization whereas the PtSn is not magnetic, in both atoms the local magnetic moment is null, this is because Sn atom transfers electric charge to Pt atom and it is equally distributed between the majority orbitals and minority orbitals. Besides we can notice that the value of E_b increases with the atomic number and takes the largest value for the PtSn nano-alloy, indicating the stability for this bimetallic cluster; furthermore the bond length shows a decreasing value with the atomic number, the largest value is present for Sn dimer whereas the minimum bond length is present for Pt_2 cluster, these results are basically due to the difference that exists in the atomic radius, being greater for Sn atom and this leads to a long bond length.

But to determine that the Pt-Sn bond is energetically favorable over the Sn_2 and Pt_2 bonds, we calculate the excess energy (E_{ex}) given by:

$$E_{ex} = E(PtSn) - \frac{1}{2}E(Sn_2) - \frac{1}{2}E(Pt_2),$$

where the terms of the equation represent the total energy of dimers involved. Our result is -1.494 eV, indicating that the mixing of Pt and Sn atoms is energetically favorable.

In this study we have considered the electronic affinity ($EA = E_0 - E_-$), the ionization potential ($IP = E_+ - E_0$), and the chemical hardness ($\eta = \frac{1}{2}(IP - EA)$).

Table 1. Our GGA-PBE results for average magnetic moment (M), in units of magneton of Bohr; binding energy per atom (E_b) in eV/atom, the bond length (L) in Å, the electronic affinity (EA) in eV, the ionization potential (IP) in eV and the chemical hardness (2η) in eV.

Dimer	M	E_b	L	EA	IP	2η
Sn ₂	2.00	1.13	2.82	1.25	6.71	5.46
Pt ₂	2.00	1.58	2.34	1.88	8.94	7.06
PtSn	0.00	2.11	2.41	0.80	7.58	6.78

For PtSn dimer, the electronic configurations for Sn is $5s^{1.77}5p^{1.66}$ and for Pt atom is $5d^{9.01}6s^{1.56}$ we can see that in the bonding in PtSn the sp electrons in Sn and the 6s electrons in Pt are the main participants in the bonding between the atoms.

In figure 1 we present the global minimum structures for pure Pt clusters and Sn clusters, we present the value of the binding energy per atom (E_b), the total magnetization (M), the average bond length (L) and the value of the local magnetic moments. For Pt clusters our ground state (GS) structure with 3 atoms agree excellently with that obtained [9] and [11];

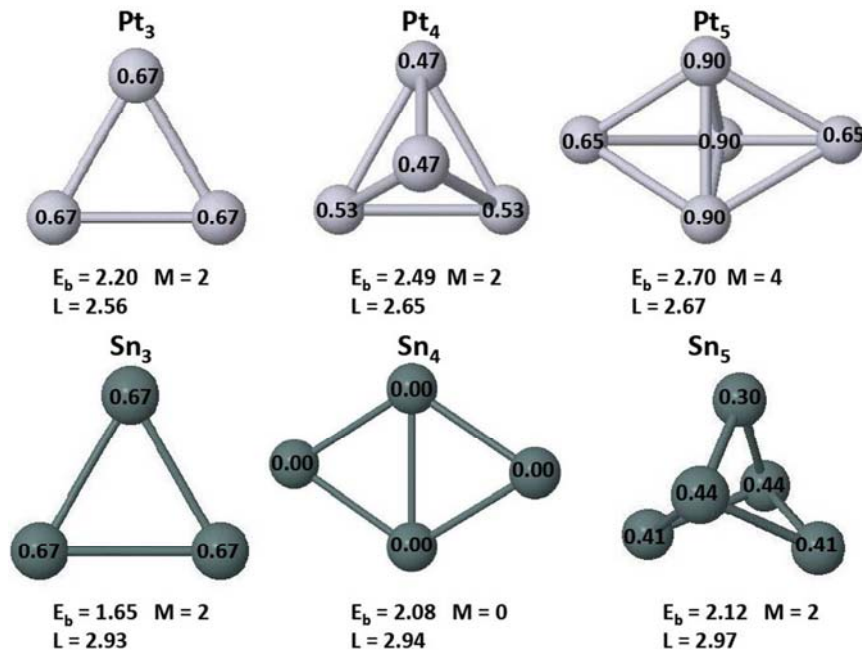


Figure 1. Lowest energy structures for pure Pt and Sn clusters obtained by our GGA-PBE approximation, we present the value of the binding energy per atom (E_b) in eV/atom, the average bond length (L) in Å, the total magnetization (M) and the local magnetic moments in units of μ_B .

For pure tin clusters, the opposite happens, our results for Sn₃ and Sn₄ present an excellent concordance with all the theoretical results and with the experiment; for Sn₃ the experimental result [12] shows a value for $E_b = 1.664 \pm 0.059$ eV/atom; for Sn₄ the experimental result [13], shows for $E_b = 1.947 \pm 0.036$ eV/atom; and for Sn₅ cluster the experiment [13] gives a value for the binding energy per atom of $2.056 \pm$

although there are differences in the values of E_b and L ; by embedded atom model [9] the binding energy per atom is 2.45 eV/atom and 2.41 Å, respectively; and by DFT techniques [11] reported an equilateral triangle with $L = 2.49$ Å, a total magnetization $M = 2 \mu_B$; our result for E_b is low and our result for L is greater than those reported. In reference [10] by using DFT scheme as implemented in VASP code found an equilateral triangle with a $E_b = 3.13$ eV/atom and $L = 2.465$ Å, and $M = 0 \mu_B$.

For Pt₄, [10, 11] reported a three-dimensional structure; in the first reference the GS corresponds a tetrahedron with $L = 2.46$ Å, a bent rhombus with $L = 2.51$ Å, and a value of M of $4 \mu_B$ was reported [11]; whereas [10] reported a planar rhombus as their GS structure with $L = 2.51$ Å and $M = 4 \mu_B$ and $E_b = 3.44$ eV/atom; our result corresponds to a non-regular tetrahedron as is reflected in the value of the atomic magnetic moments.

For Pt₅, the DFT results, [10, 11], show a side capped square; both references reported a value of $M = 2 \mu_B$ and Sebetci obtained a triangular bipyramid [9], as well as our result, although our GS is a non-regular structure, reference [11] found this geometry with $M = 4 \mu_B$ as their first isomer. Our results in all these structures, the local magnetizations are parallel the magnetic order in the cluster is ferromagnetic-like.

0.046 eV/atom; although these experiments do not show value for M , by using DFT scheme as implemented in VASP code [17], report GS with a null total magnetization; from figure 1 our GS for Sn₃ and Sn₅ clusters present a value of $M = 2 \mu_B$.

All our results coincide with all those that are published in the literature, using DFT techniques implemented in different computer packages. [14] report results using the Dmol code;

the plane wave methods implemented in VASP code [15]; a combination of genetic algorithm with the plane wave method (VASP) was used in [16, 17]. All these studies obtain the same ground state for Sn clusters in this size range considered here. With these results we can assure the reliability of *our* theoretical method and apply it to the study of PtSn nanoalloys.

3.1. PtSn Nanoalloys

In this section we present our GGA-PBE results for Pt_xSn_y clusters with $x + y \leq 5$. Figure 2 show the lowest energy

geometries for our nanoalloys considered in this study. As was mentioned above, our calculations show an electric charge transference from Sn atoms to Pt atoms, the largest transference is in Pt_4Sn cluster and the smallest in Pt_2Sn_3 cluster; in the first case, the charge is distributed almost equally between the majority orbitals and minority orbitals in Sn atom, on the other hand in the Pt_2Sn_3 , the electric charge is preferentially distributed in the majority orbitals (spin-up).

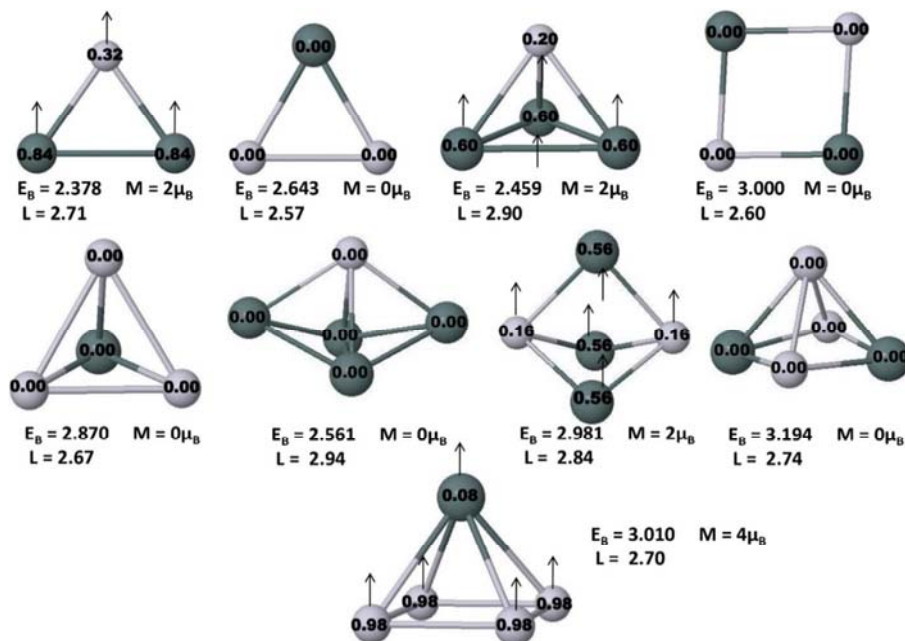


Figure 2. Global minimum structures for Pt_xSn_y obtained by our GGA-PBE approximation, we present the value of the binding energy per atom (E_b) in eV/atom, the average bond length (L) in Å, the total magnetization (M) and the local magnetizations, both in units of μ_B . The clear circles represent the Pt atoms and the other circles represent the Sn atoms.

3.2. Stable Geometries

We can notice, from figure 2, that for nanoalloys rich in Sn atoms, they usually present the lowest value in E_b as well as the largest L , this can be understood due to the large atomic radii for Sn atom, leading to structures with atoms having large inter-atomic distances. For nanoalloys with 3 atoms, in both structures the ground states correspond to an isosceles triangle; in PtSn_2 the Sn-Sn bond is 2.97 Å and the Pt-Sn bond length is 2.58 Å whereas for Pt_2Sn all the bond lengths are very similar in their values, Pt-Pt bond of 2.56 Å and the Pt-Sn bond of 2.58 Å for these clusters, the large bond length Sn-Sn, indicates the weakness of the bond.

For 4 atoms, only one nanoalloy, Pt_2Sn_2 , present a planar geometry very similar to a rhombus where each Pt(Sn) atom is connected to two Sn(Pt) atoms, the Pt-Sn bond length is 2.60 Å. This structure is reported in [22], their Pt-Sn bond length is 2.57 Å, and their E_b is 3.204 eV, the other nanoalloys have the same three-dimensional geometry, a regular tetrahedron. For PtSn_3 , the Sn atoms form an equilateral triangle whose size is of 3.11 Å, whereas the Pt-Sn bond is 2.70 Å in this geometry, the small bond length of

Pt-Sn indicates a strong bond and the weakness for the Sn-Sn bonds.

On the other hand, the Pt_3Sn cluster is a regular tetrahedron where the Pt-Pt bonds are of 2.67 Å and the Pt-Sn inter-atomic distance is 2.68 Å, this structure was obtained in [22] by using a genetic algorithm combined with density functional theory implemented in Dmol program, they obtained $E_b = 3.148$ eV/, a largest value compared with our result, see figure 2.

We can notice that in that size, there is a jump of 0.541 eV in the binding energy per atom when changes the concentration of Sn atoms in nanoalloy, i.e., from PtSn_3 cluster to Pt_2Sn_2 cluster; this jump is attributed to the transition from a three-dimensional geometry to a planar geometry.

Finally, for clusters with 5 atoms, we can notice the absence of planar geometries in the global minimum structures, the geometric arrangement of the atoms goes from a tetrahedron capped to a square pyramid; we can notice that the behavior of the average bond length is very similar to that previous cases, see figure 2, i.e., the value of L decreases as the number of Sn atoms in the nanoalloy decreases.

The different Pt-Sn bond lengths in the clusters; depend of the number of Sn atoms in the nanoalloy, for nanoalloy rich in Sn atoms, the Pt-Sn average bond length is 2.84 Å, 2.69 Å, for Pt₂Sn₃; 2.69 Å, for Pt₃Sn₂, and 2.74 Å, for the nanoalloy rich in Pt atoms; whereas the Sn-Sn average bond length is 2.92 Å for PtSn₄ cluster.

3.3. Magnetic Behavior

A few nanoalloys studied in this work present magnetism, i.e a non zero value for M. In figure 2, we show the value of the local magnetic moments of the different non-equivalent atomic sites; we can notice that a few nanoalloys present magnetic behavior, where the atomic moments are aligned giving a ferromagnetic-like order into the cluster; we can see, that in each size, there are at least one cluster with magnetic order. For clusters with 3 atoms and 4 atoms, the Sn atoms give the main contribution to M.

For clusters with 3 and 4 atoms, we can notice that nanoalloys with only one Pt atom in the structure have a value of M different of zero and also the main contribution to M comes from the Sn atoms; besides, in this range of size the value of $\mu(\text{Pt})$ decreases when the number of neighboring Sn atoms increases, see figure 2.

For nanoalloys with 5 atoms the magnetic behavior is somewhat different, now PtSn₄ cluster does not present a value for M and all the atoms have a null local magnetizations, in the nanoalloys with a value of M different from zero, the magnetic order remains ferromagnetic-like; in nanoalloys with magnetism the value of $\mu(\text{Pt})$ presents a similar behavior that in the previous case, increases with the decrease in the number of tin atoms; in this range of size, Pt₄Sn cluster present the largest value in M and the main contribution is given by the local magnetic moments in Pt atoms; as was mentioned above, in this cluster exist the largest transfer of electric charge, so that the 5s orbitals in the tin atom are equally occupied, both majority ($5s^{0.84}$) and minority ($5s^{0.84}$) orbitals, so the 5p electrons are the ones that give the value of the magnetic moment in the Sn atom; the majority orbitals have the electronic configuration $5p^{0.84}$, and the electronic configuration in the minority orbitals is $5p^{0.76}$.

3.4. Stability

As in the case of PtSn dimer, we can determine if the mixing of atoms is energetically favorable or in other words, we can determine if the Pt-Sn bonds are favorable in energy over the Pt-Pt bonds and Sn-Sn bonds, this through the excess energy defined by:

$$E_{\text{ex}} = E(\text{Pt}_x\text{Sn}_y) - (x/N) E(\text{Pt}_N) - (y/N) E(\text{Sn}_N)$$

where the first term in this equation represents the total energy in the nanoalloy, and the other two terms represent the appropriate fraction of the total energy of the respective pure clusters; N is the number of atoms in the nano alloy, and $x + y = N$. A negative value of E_{ex} indicates a favorable mixing of atoms.

In figure 3 we show the value of E_{ex} , and depends of the size of the cluster, we can notice that the mixing of atoms

is favorable in all the concentrations considered in this work, moreover the clusters rich in Sn have the lowest modulus of the excess energy, as in E_{b} , because these structures are very open due to the great atomic radio of tin atom. Another fact that we can notice is that the nanoalloys with a single Sn atom have the second lowest value in the modulus of E_{ex} , therefore the mixing of atoms is more favorable for those structures not rich in Pt or Sn atoms. In addition, these results are congruent with the E_{b} results, for example, for nanoalloys with 4 atoms, Pt₂Sn₂ has the highest E_{b} and the highest absolute value of E_{ex} ; from figure 2 and figure 3, we can see that this fact is almost maintained in nanoalloys with 5 atoms.

3.5. Electronic Properties

In this section, we present for all the clusters considered here, the vertical electronic properties such as ionization potential (IP), electron affinity (EA) defined by: $\text{IP} = E_+ - E_0$; $\text{EA} = E_0 - E_-$ depending on the concentration of Pt atoms in the cluster.

In these equations, E_0 is the total energy of the neutral clusters and E_+ and E_- represent the total energy of the structures with a positive electric charge and with a negative electric charge respectively. The value of IP indicates the easiness of the system to lose an electron, i.e., for high (low) values of IP, it is more difficult (easy) for the system to lose one electron; whereas lower values of EA reflects the ease of a system to accept an electron.

In table 1, we show values of EA and IP for dimers involved in this study; we can notice that Pt₂ is a bad receiver of electronic charge, but the mixing of atoms favors the reception of electrons; similarly, Pt₂ it is a bad electron donor, but now the mixing of atoms does not favor the donating atoms; the best donor of electronic charge is Sn₂.

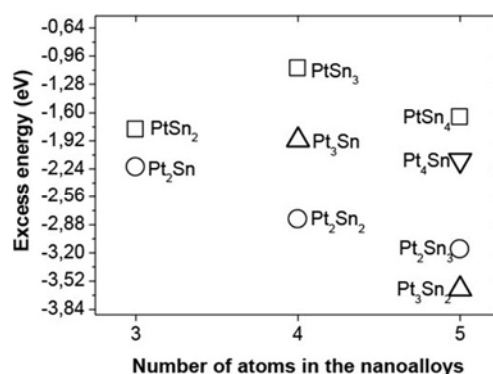


Figure 3. Excess energy for global minimum the Pt_xSn_y nano alloys considered in this study.

In figure 4, we present the behavior of EA, IP and Hardness for pure clusters and nanoalloys. In the first row we show EA both the pure clusters and for the bimetallic clusters. We can see that for Pt clusters, EA increases with the size of the cluster, being the best receiver of electronic charge Pt₃ cluster; whereas for Sn clusters, Sn₃ and Sn₄ are the best receivers of electrons except for Sn₅, this structure is the worst receiver of electrons.

For Pt_xSn_y nanoalloys, mixing atoms favors, in some cases, the reception of electrons; for $x + y = 3$, the value of EA is lower than Pt_3 and Sn_3 , although we should note the highest value of EA is for the structure rich in Pt atoms, but even so it is slightly lower than of pure clusters.

For clusters with 4 atoms, the best receiver of electronic charge is Sn_4 in approximately 0.2 eV; mixing atoms favors the reception of electrons except for PtSn_3 cluster.

For pure clusters with 5 atoms, the best receiver of electrons in Pt_5 approximately by 0.15 eV with respect to Sn_5 cluster; for bimetallic clusters the best receivers of electronic charge are clusters with 1, 2 and 3 Pt atoms, their EA is lower than the respective EA for pure clusters, see figure 4.

For ionization potential, its behavior is shown in the

middle panel of figure 4, for Sn clusters, IP decreases with the number of atoms in the cluster increases, we can see that Sn_5 is the best electron donor; whereas for Pt clusters, the behavior of IP is with a kind of concavity upwards, and the cluster with the lowest value of IP is Pt_4 ; in the same middle panel of figure 4, we show IP for nanoalloys. The IP value depends on the concentration of Pt atoms in the nanoalloy; for nanoalloys rich in Pt, the ionization potential value is the highest in all the sizes considered in this study, also for nanoalloys rich in Sn atoms the opposite case is presented, these nanoalloys have a lower value than the corresponding pure clusters; but we can also see that the bimetallic cluster which is the best charge donor is Pt_2Sn_3 .

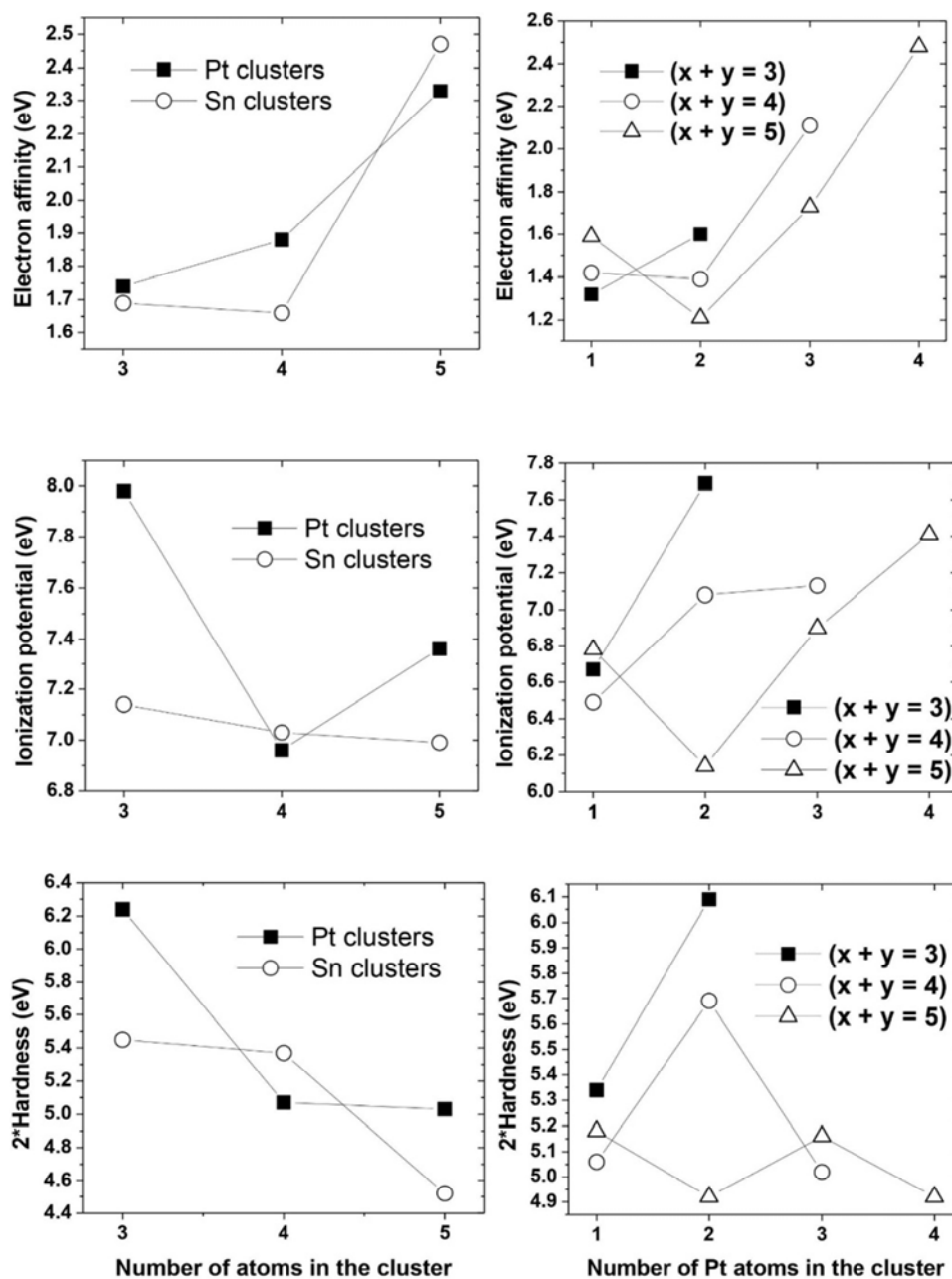


Figure 4. Electronic properties for the pure Pt and Sn clusters and for the nano alloys considered here.

Both quantities (IP and EA), are related to the chemical hardness (η) which is an index for chemical reactivity, and is defined as: $\eta = 1/2 (IP - EA)$. The values of the chemical hardness are plotted in the lower panel of figure 4.

From this point of view, the nanoalloys with the lowest chemical reactivity are those with the greatest value of the chemical hardness. For tin and Pt pure clusters the chemical reactivity decreases with nanoparticle size, although Pt clusters with 4 and 5 atoms, the reactivity is maintained at the same value. In general, from the figure 4, we can see that Sn_5 is the most reactive due to its low hardness value.

The mixing of atoms, modifies the behavior of chemical reactivity, some bimetallic clusters, Pt_2Sn and Pt_2Sn_2 , have a high value in hardness than in pure clusters, making them clusters with low reactivity.

The rest of the structures, their hardness value is included in the same range as that of pure clusters, but there are certain characteristics specific to nanoalloys; but still, our results show a dependence of the hardness with the number of Pt atoms, i.e., compares the stability of a structure with that of its neighbors. For nanoalloys with 4 atoms, the reactivity is higher when there is an odd number of Pt atoms in the structure; an interesting feature is present for nanoalloys with 5 atoms, the hardness has a quasi-oscillatory behavior, but in this case the higher reactivity is present in nanoalloys with an even number of Pt atoms. This oscillatory behavior has been found in small CoCu nanoalloys [23]. In general terms, the nanoalloys with 5 atoms are the ones with the best chemical reactivity.

4. Conclusions

We have carried out a DFT-GGA calculations for the ground state structures, stability, magnetism and electronic properties of small binary Pt_xSn_y nanoalloys with $x + y \leq 5$ atoms; the study was done by using density functional theory techniques using SIESTA code, we present our main conclusions.

The lowest energy structures present geometries where atoms have a high coordination, and we find a flat geometry only in structures with 4 atoms; mixing Pt atoms with Sn atoms favors the formation of the nanoalloys, those rich in Sn atoms present the lowest modulus of the excess energy, all the Pt_xSn_y clusters present a general trend, the binding energy per atom is decreasing when the concentration of tin atoms in the structure is increasing; mixing atoms does not notably favor magnetism, since the total magnetization takes low values and the few structures with magnetic behavior present a ferromagnetic-like order but properties that are benefited by the mixing of atoms, are the electronic affinity and the ionization potential, since most of the nanoalloys considered here have lower values than those that correspond to pure clusters. In the size range considered in this study our result allows us give a classification as good or bad catalysts, by the value of chemical hardness, high values indicate bad catalysts, Pt_2Sn and Pt_2Sn_2 , can be considered as bad catalysts, whereas Pt_3 and Sn_5 have the lowest hardness,

because of this they can be considered good catalysts.

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