Effect of Ni and Pd on the Geometry, Electronic Properties, and Active Sites of Copper Clusters

Elizabeth Florez,[†] Fanor Mondragón,*,[†] and Patricio Fuentealba[‡]

Institute of Chemistry, University of Antioquia, A.A. 1226, Medellín, Colombia, and Department of Physics, University of Chile, Las Palmeras 3425, Ñuñoa, Santiago, Chile

The geometry, electronic properties, and active sites of copper clusters doped with Ni or Pd atoms, $Cu_{n-1}M$ ($n = 2$−6; M = Ni, Pd) have been investigated using first-principles methods. Planar structures are energetically favorable in $Cu_{n-1}Ni$ ($n = 2$−6). However, for Pd-doped clusters, three-dimensional structures are competitive in energy, and for $n = 6$, the most stable structure is not planar. Several properties of doped copper clusters present odd−even oscillations as the number of copper atoms grow. The different atomic ground-state configuration of Ni and Pd determines the bonding and electronic properties of doped copper clusters. The interaction between impurities and copper atoms can modify the chemical hardness and active sites of doped copper clusters markedly inducing directionality in the reactivity. This effect is relevant to the behavior of catalysts as well as in the growth of metallic films.

1. Introduction

Several studies have shown that bimetallic systems present better catalytic properties with respect to pure metals, such as selectivity, stability, and activity.[1−5] For this reason, bimetallic systems have been used in different industrial processes.[6−10] In particular, in the catalytic processes the bimetallic systems containing metals of the group 10 (Pt, Pd, or Ni) and "host metals" like Cu have been used in many reactions such as hydrocarbon catalytic combustion;[11] CO,[12] benzene,[13] and CO_2[14] hydrogenation; NO_x reduction,[15] and so forth

The different activity of bimetallic systems with respect to the monometallic systems has been attributed to two effects. One is the "bifunctional effect−ensemble" which is the change of the geometry of the bimetallic systems with respect to the monometallic systems, and the other is the "ligand or electronic effect" which suggests that electronic properties of the pure metal are modified by the addition of the second metallic component.[16−18] The concepts of structural and electronic effects have been very useful to justify the superior catalytic activity of the bimetallic systems. The study of both effects has become an important area of research both experimentally[16,19−21] as well as theoretically.[18,22,23]

Although experimentally quite useful information has been obtained, it has been very difficult to determine the role of each one of the above-mentioned effects. Therefore, computational tools have been proposed as a useful methodology to obtain details of the electronic properties of mono- and bimetallic clusters and the relation to their chemical reactivity. Many theoretical papers on bimetallic systems have been published.[22−24] These studies are based on the knowledge of the electronic and ensemble effects on the chemical reactivity. For example, Illas et al.[22−24] have shown that these effects can modify the chemical reactivity of bimetallic systems toward probe molecules. The studies correspond to the dissociation of H_2 on RhCu surfaces,[22] interaction of molecular hydrogen with the PdCu (111) surface,[23] and chemisorption of CO on the RhCu surface.[24]

Nevertheless, to our knowledge, there are no studies in bimetallic systems aimed at predicting the nature of their active sites. Previous investigations in our group showed that theFukui function, approximated as the square of the HOMO orbital, and the condensed Fukui function, taken as its integration over the basins of the Fukui function itself, are useful tools to predict the active sites of copper clusters which can react with molecular oxygen. The so-defined Fukui function is also able to predict the site of growth of metallic clusters.[25] Reactivity descriptors such as chemical hardness (η) and chemical potential (μ) have been found to be very useful tools for the characterization and understanding of electronic properties of Cu clusters.[26−28]

On the basis of those findings, the objective of the present investigation is to use the Fukui function and chemical hardness to study the variations of the active sites and electronic properties of copper clusters, Cu_n ($n = 1$−6), when one atom of Ni or Pd is added to the cluster to form the bimetallic systems $Cu_{n-1}Ni$ or $Cu_{n-1}Pd$. In addition to this, changes in other properties such as geometry, total bond order, and atomization energy of the bimetallic clusters are also investigated.

2. Methodology

In this section, we present a brief description of the reactivity descriptors used in this work. Density functional theory (DFT)[29−31] has provided the basis for rigorous mathematical definitions of reactivity descriptors such as chemical potential (μ), chemical hardness (η), Fukui function ($f(r)$), electrophilicity index (ω), and so forth. The information given by these parameters has been used successfully in the analysis and characterization of different kinds of molecular structures and chemical reactions.[32−37]

In DFT, the molecular hardness of an *N*-electron system with total energy *E* and external potential $v(r)$ is defined as the second derivative of the energy with respect to N[31,38]

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

In numerical applications, η is calculated using the finite

* Author for correspondence. E-mail: fmondra@catios.udea.edu.co.
† University of Antioquia.
‡ University of Chile.

13794 *J. Phys. Chem. B, Vol. 110, No. 28, 2006*

Florez et al.

difference approximations as

$$\eta = \text{IP} - \text{EA} \tag{2}$$

where IP is the ionization potential and EA the electron affinity.

By using Janak's theorem,[39] the hardness can be calculated as

$$\eta = \epsilon_{\text{L}} - \epsilon_{\text{H}} \tag{3}$$

where ϵ_{H} and ϵ_{L} are the energies of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), respectively. It is important to mention that, in order to determine the hardness of a chemical system, the difference between the HOMO and LUMO energies (eq 3) has been indistinctly used with both Hartree−Fock and Kohn−Sham orbital energies.[40] The argument, which has been recently criticized,[41] is that the important point is the trend in a series of molecules or clusters and not the absolute values. However, the use of the Kohn−Sham orbital energies with the currently used exchange-correlation functionals should be done with cautious, because it is known that none of these functionals represent the correct asymptotic behavior.

Parr and Yang,[42] defined the Fukui function as

$$f(\vec{r}) = \left(\frac{\delta \mu}{\delta v(\vec{r})} \right)_N \tag{4}$$

It has been shown that, in a first approximation, the limit of this derivative is equal to the square of the respective frontier orbital, the HOMO, when the derivative is taken from the left, f^-, and to the LUMO when the derivative is taken from the right, f^+.[42] It is worth mentioning that this approximation neglects the orbital relaxation effects, which could be in some cases important. Perturbation theory should be necessary for a proper calculation of this quantity.

In the Kohn−Sham scheme, the Fukui function can be defined as[43]

$$f(\vec{r}) = \left(\frac{\delta \mu}{\delta v_{\text{KS}}(\vec{r})} \right)_N \tag{5}$$

where $v_{\text{KS}}(\vec{r})$ is the effective Kohn−Sham potential. This derivative is equal to the square of the respective frontier orbital

$$f^{\alpha}(\vec{r}) = |\phi^{\alpha}(\vec{r})|^2 \tag{6}$$

where ϕ^{α} is the frontier orbital (α = HOMO or LUMO). This is an exact equation, and the so-implemented Fukui function is a positive definite function which normalizes to unity.[44]

In a previous work,[45] the condensation of this function using a numerical integration of the Fukui function over the basins of the Fukui function itself has been proposed and named $f_{Ff}^{\pm}$ for an acceptor or donor system. In this work, this function has been used for the analysis of the mono- and bimetallic systems.

The calculations were carried out solving the Kohn−Sham equations using the BLYP exchange-correlation functional.[46,47] For Cu, Ni, and Pd, the effective core potential (LANL) and a double-ζ-like basis set were used.[48] To improve the reliability of the results, the basis set was augmented with s, p, and d diffuse functions. Analytical frequencies were calculated for all stationary points to ensure that they are not saddle points. The structures of the bimetallic clusters characterized in the present research were selected under two criteria. First, the position of the Pd or Ni atom was chosen from the Cu clusters growth pattern reported by Cheng et al.,[49] and as a second criterion,

the structures of the most stable isomers published in the scientific literature.[50,51]

Hence, only the isomers corresponding to true minima are presented. Values are not corrected for basis set superposition errors, and the zero-point energy is not included. All the calculations were performed using the *Gaussian 03* package.[52] The Fukui function was evaluated using a modified version of the Top-Mod program.[53]

3. Results and Discussion

The determination of the electronic ground state of the transition metals is particularly difficult mainly due to two reasons. One is the large number of isomers and the other one is the abundance of low-lying electronic states due to the incomplete d-shell filling. On the other hand, in the calculation of physical and chemical properties of transition metals, electron correlations and relativistic effects play a fundamental role. To partially account for these effects, DFT combined with the use of relativistic effective core potentials have been used and have been shown to be important tools to investigate these systems.

For the purpose of defining the computational approach to be used in this study, we determined the atomization energies, D_o, of the dimers Cu_2, CuNi, and CuPd using BLYP and B3LYP functionals and compared these results with experimental data (Table 1). The calculated D_o energies with the BLYP functional are in better agreement with experimental results.[54−58] However, it was observed that the B3LYP hybrid functional underestimates these values. Therefore, the functional BLYP was chosen as the calculation method in this study.

Geometry. In Figures 1, 2, and 3, the lowest-energy structures and some lower-lying isomers of the Cu_n, $Cu_{n-1}Ni$, and $Cu_{n-1}Pd$ are presented. The bond lengths of Cu_2, CuNi, and CuPd are 2.27, 2.26, and 2.39 Å, respectively, and the bond energies are 2.14, 2.09, and 1.64 eV, respectively. These results show that the Cu−Cu and Cu−Ni bonds are similar, whereas the Cu−Pd bond is clearly weaker. The optimized ground-state structures of Cu_2Ni and Cu_2Pd, 2-Ni and 2-Pd, as presented in Figure 1, have C_{2v} symmetry with apex angles of 148.2° and 58.7°, respectively. Cu_3Ni and Cu_3Pd have C_{2v} rhombus ground states (3a-Ni and 3a-Pd). Some "Y-shaped" lower-lying structures are obtained with the doping atom occupying the center or apex positions. Above their lowest-energy structures, two optimized configurations with C_{2v} rhombus, 3b-Ni and 3b-Pd, have been found. They are 0.09 and 0.26 eV above the ground state, respectively. In the case of Cu_4Ni and Cu_4Pd, their most stable structures are planar trapezoidal shaped. The isomers 4b-Ni and 4b-Pd are 0.18 and 0.11 eV above the ground states, respectively. For Cu_5Ni and Cu_5Pd, three lower-lying energy isomers are presented in Figure 3. For Cu_5Pd, the most stable structure takes a side-capped trigonal bipyramid shape, 5a-Pd. For Cu_5-Ni, the most stable isomer is triangular in geometry, and it has C_{2v} symmetry, 5a-Ni.

In general, Cu_n and Cu_nNi clusters prefer planar configurations arrays. For $Cu_{n-1}Pd$, the geometries depend on their size, i.e., $Cu_{n-1}Pd$ ($n \leq 5$) are more stable as the planar configuration, while increasing Cu content favors 3D structures. The most stable structures obtained here, with $n \leq 5$, for Pd-doped clusters are in agreement with published DFT calculations.[51] For $Cu_{n-1}Ni$ and $Cu_{n-1}Pd$, and $n < 5$, analogous planar configurations with the same order of stability have been found in the Au_nNi and Au_nPd[59] series of clusters.

Atomization Energy (D_o) and Total Bond Order. The binding energies or atomization energies (D_o) have been calculated for the monometallic clusters as $D_o = [E(Cu_n) - $

Cu Clusters Doped with Ni or Pd Atoms

J. Phys. Chem. B, Vol. 110, No. 28, 2006 **13795**

TABLE 1: Comparison of Bond Lengths (in Å) and Dissociation Energies (in eV) between Calculated (BLYPm B3LYP) and Experimental Data of the Ground State of Transition Metal (M_2) Clusters
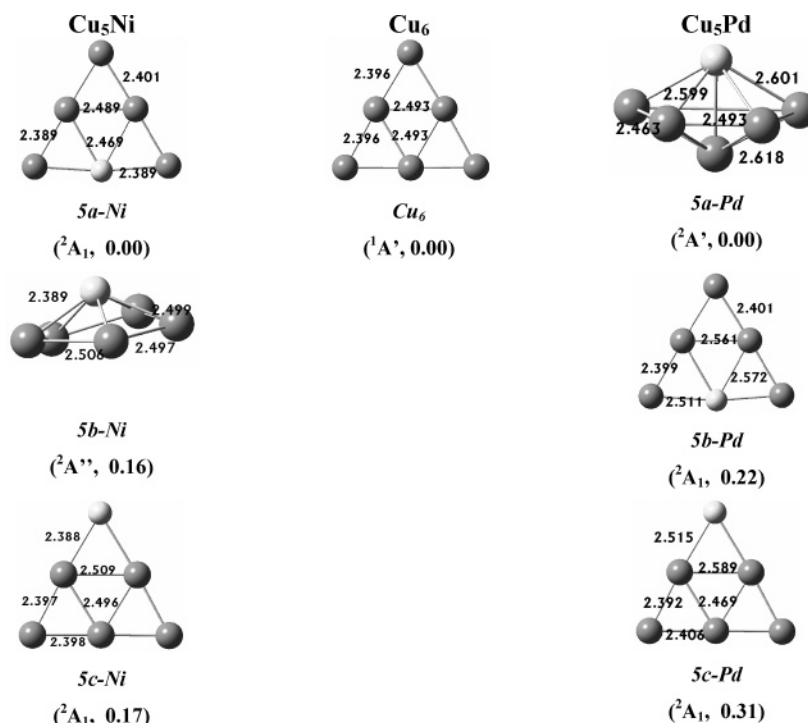
parameters	$Ni_2(^3\Sigma_g^+)$			$Cu_2(^1\Sigma_g^+)$			$Pd_2(^3\Sigma_g^-)$		
	BLYP	B3LYP	exp	BLYP	B3LYP	exp	BLYP	B3LYP	exp
R (Å)	2.13	2.09	2.200^a	2.26	2.27	2.22^c	2.53	2.55	
D_o (eV)	2.54	1.24	$2.068^a \pm 0.01$	2.15	1.95	2.08^d	1.08	0.76	$1.026^e \pm 0.155$
			$2.36^b \pm 0.2$						

[a] From ref 53. [b] From ref 54. [c] From ref 55. [d] From ref 56. [e] From ref 57.
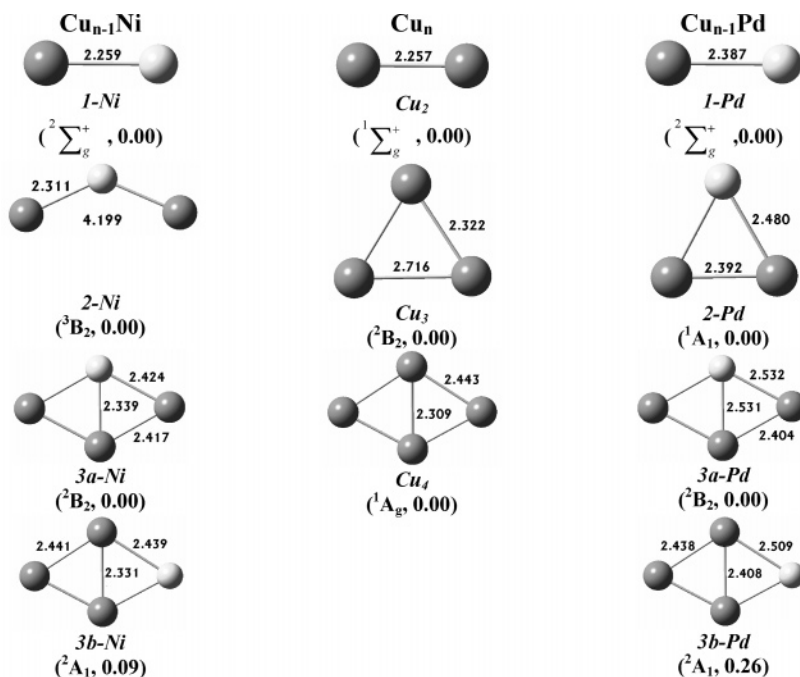
Figure 1. Optimized ground-state geometries of $Cu_{n-1}Ni$ and $Cu_{n-1}Pd$ ($n = 2-4$) clusters. Indicated distances in Å. Values in parentheses refer to electronic ground states and to relative energies, in eV, of lower-lying energy structures with respect to the corresponding ground-state structures.
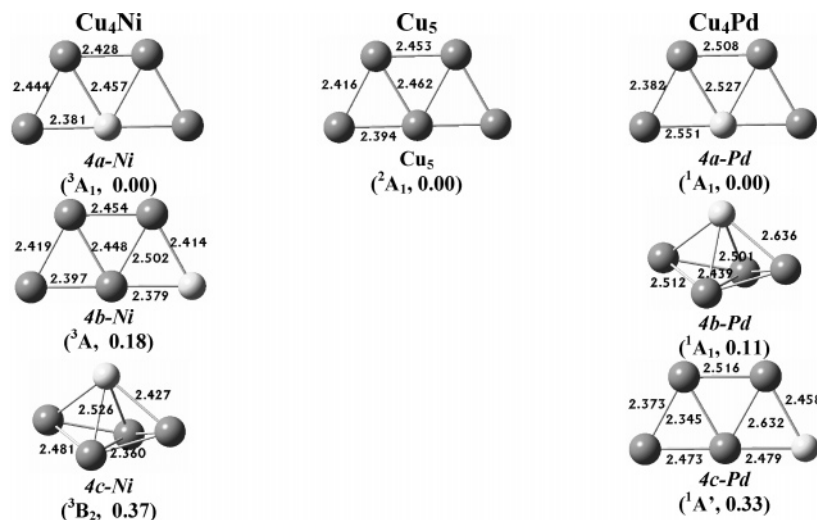
Figure 2. Optimized ground-state geometries of Cu_4Ni, Cu_5, and Cu_4Pd clusters. Indicated distances in Å. Values in parentheses refer to electronic ground states and to the relative energies, in eV, of lower-lying energy structures with respect to the corresponding ground-state structures.

$nE(Cu)]$ and for the bimetallic systems Cu_nM as $D_o = [E(Cu_nM_m) - nE(Cu) - E(M)]$. The results, in eV, are reported in Figure 4a. It is observed that the bimetallic systems present a D_o energy slightly more stable than the monometallic system of the same size. Therefore, it shows that the Ni and Pd atoms can enhance the stability of doped copper clusters with respect to pure copper clusters.

To discuss the bonding strength, the total bond order (see Figure 4b) using the natural bond orbital approximation[60] has been calculated. The order of bonding strength of the corresponding doped cluster is Ni > Pd. The $Cu_{n-1}Ni$ series presents odd−even oscillations, while this behavior is not observed in the $Cu_{n-1}Pd$ series. Furthermore, the Ni-doped clusters with an even number of copper atoms present a stronger bond interac-
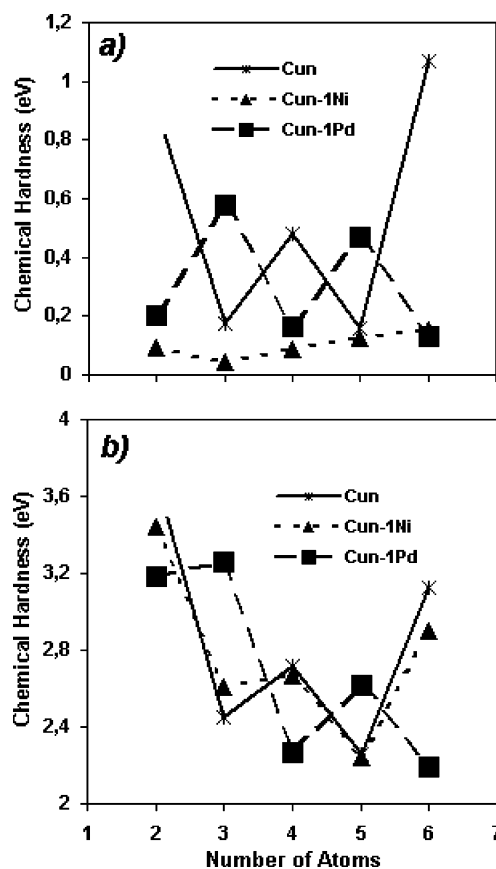
Cu₅Ni　　　　　**Cu₆**　　　　　**Cu₅Pd**

5a-Ni
($^2A_1$, 0.00)

Cu₆
($^1A'$, 0.00)

5a-Pd
($^2A'$, 0.00)

5b-Ni
($^2A''$, 0.16)

5b-Pd
($^2A_1$, 0.22)

5c-Ni
($^2A_1$, 0.17)

5c-Pd
($^2A_1$, 0.31)

Figure 3. Optimized ground-state geometries of Cu₅Ni, Cu₆, and Cu₅Pd clusters. Indicated distances in Å. Values in parentheses refer to electronic ground states and to relative energies, in eV, of lower-lying energy structures with respect to the corresponding ground-state structures.
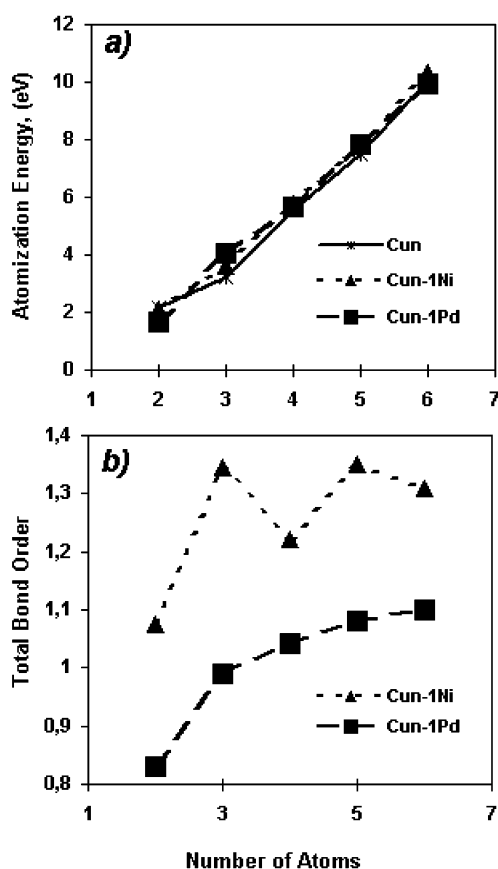
Figure 4. Calculated (a) atomization energies and (b) total Cu$_{n-1}$Ni and Cu$_{n-1}$Pd bond orders.

Figure 5. Effect of Ni and Pd on the calculated (a) chemical hardness $\eta^{(H,L)}$ and (b) chemical hardness $\eta^{(IP,EA)}$ of copper clusters.

tion, which is due to the participation of the two s-electrons of the Ni atom. The bonding properties of bimetallic clusters should be attributed to the different bonding interaction between the doping elements and the copper atoms originated from the different atomic ground states of impurity atoms.

Chemical Hardness and Fukui Function. Figure 5a shows the behavior of chemical hardness for Cu$_n$, Cu$_{n-1}$Ni, and Cu$_{n-1}$Pd clusters obtained using Janak's theorem, $\eta = \epsilon_L - \epsilon_H$, while ϵ_H and ϵ_L are the energies of the HOMO and the LUMO, respectively. Chemical hardness is an electronic quantity
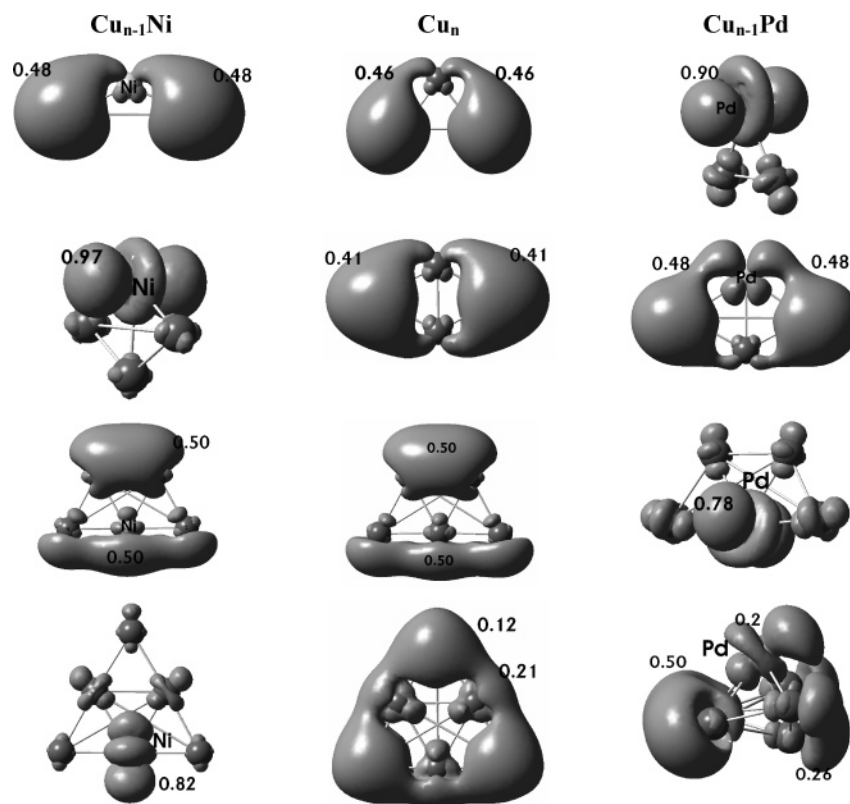
Figure 6. Donor Fukui Function f_{Ff}^{-} of $Cu_{n-1}Ni$, Cu_n, and $Cu_{n-1}Pd$ in their ground states.

that has been used previously to characterize the relative stability of clusters of Cu and Na.[26,61] The higher the value of the hardness, the more stable the system becomes. Also, the chemical hardness can be seen as inversely proportional to a charge transfer. Therefore, it is expected that clusters with a minimum value of hardness are able to transfer charge to another system.

In Figure 5a, it can be seen that the hardness of bimetallic systems is smaller than that of the respective monometallic clusters, suggesting that the presence of Ni and Pd impurities can be a useful method to optimize the catalytic properties of copper clusters.

On the other hand, odd−even alternations are markedly shown in pure and Pd-doped copper clusters. However, in $Cu_{n-1}Ni$, no even−odd alternation is found. The even−odd alternation in copper clusters can be explained on the basis of the electronic cluster structure. In the case of clusters with an even number of atoms, all electrons are paired giving a closed-shell electronic structure with the highest chemical hardness. In contrast, all odd-numbered clusters have a very small hardness with the HOMO occupied by a single electron. For $Cu_{n-1}Ni$ and $Cu_{n-1}Pd$, the different behavior of chemical hardness is related to different atomic properties of doping atoms in the ground state and lower-lying excited states. The Ni atom presents two almost degenerated states, $3d^8 4s^2$ and $3d^9 4s^1$. Therefore, one or two electrons can contribute to the stability of Ni-doped Cu clusters, and therefore, doublet and triplet states can be found in Ni-doped copper clusters. However, in the case of the Pd atom, the promotion energy from $4d^{10}$ to $4d^9 s^1$ is 0.95 eV, and for small clusters, only one electron can participate in the bonding to the copper cluster. Hence, the $Cu_{n-1}Pd$ clusters with an odd number of atoms present a spin doublet state, whereas the clusters with an even number of atoms are in a singlet state. Therefore, the even−odd oscillation in the gap of $Cu_{n-1}Pd$ clusters is due to the singlet−doublet oscillation, which

is not present in the case of $Cu_{n-1}Ni$ clusters because these clusters are triplet−doublet open-shell type.

It is important to mention that sometimes when the energy gap is small the orbital energies are not appropriate to determine the hardness. In such cases, there is more than one orbital contributing to the hardness, and the use of the vertical ionization potential and vertical electron affinity, eq 2, are better options. Figure 5b presents the hardness calculated in this way. In comparison with Figure 5a, one can see for the Cu_n and $Cu_{n-1}Pd$ series of clusters that the behavior of the hardness is similar using any of the two ways to calculate it. However, for the $Cu_{n-1}Ni$ series, in one case the value is almost constant ($\eta^{(H,L)}$), while in the other case ($\eta^{(IP,EA)}$), it presents oscillations.

It can be concluded from these results that Cu_n and $Cu_{n-1}Pd$ clusters present similars even−odd oscillations as a function of the cluster size. These oscillations are easily explained by the nature of the electronic shell of these systems (open−closed). Cu_n and $Cu_{n-1}Pd$ clusters with closed-shell (with *n* even) are harder than open-shell clusters (*n* odd) and therefore more stables. For the $Cu_{n-1}Ni$ clusters, there are no even−odd alternations, because all the clusters are open-shell independent of *n*. The lack of oscillations found for $Cu_{n-1}Ni$ clusters are also present in the IP study for Ni_n clusters.[62]

On the other hand, it has been shown that the condensed Fukui function is able to predict the possible binding site of an oxygen molecule on a copper cluster.[25] Hence, the reactivity of the three series of clusters has been evaluated using the condensed Fukui function, f_{Ff}^{-}. The results are shown in Figure 6. The numbers in the figure are the f_{Ff}^{-} values. In each cluster, the regions of higher values of f_{Ff}^{-} are assigned as active regions for the reactions with gas molecules, such as O_2. The region of lower values of f_{Ff}^{-} are assigned as inactive regions. An important change in the reactivity among the bare copper clusters and the doped ones can be observed. For the mono-

metallic systems, the reactivity is almost always delocalized into the whole cluster, whereas in the bimetallic clusters, the foreign atom induces localization of the electronic density in one or two atoms. The trend between the $Cu_{n-1}Ni$ and $Cu_{n-1}Pd$ series of clusters is very different. For the clusters with an odd number of atoms, the reactivity is localized in the Pd atom, whereas in the $Cu_{n-1}Ni$ series, the reactivity is localized at the copper atoms. The clusters with an even number of atoms present just the opposite behavior. It is also worth noting the marked d-character of the Fukui function when the reactivity is localized in the doped atom. In addition, as expected, this effect induces directionality in the reactivity of these systems. Therefore, it is possible to foresee the active sites for the growth of the cluster.

4. Conclusions

The geometric and electronic properties and active sites of Ni- and Pd-doped copper clusters have been investigated using first-principles methods and compared with the properties of the bare copper clusters. The planar structures are energetically favorable for all the studied $Cu_{n-1}Ni$ ($n = 2-6$) clusters, whereas the Cu_5Pd cluster presents a 3D structure as the most stable configuration. The different atomic ground-state properties of Ni and Pd atoms are important in determining the electronic and bonding properties and the positions of the active sites of doped copper clusters. Ni atoms can donate one or two electrons to copper clusters, while Pd only contributes one electron through the promotion of one electron from 4d to 5s. The analysis of the Fukui function shows that the presence of a doping atom like Ni or Pd can change in a significant way the reactivity of copper clusters, inducing directionality to the reactive sites.

References and Notes

(1) Clarke, J. K. A. *Chem. Rev.* **1975**, *75*, 291.
(2) Sinfelt, J. H. *Acc. Chem. Res.* **1977**, *10*, 15.
(3) Sinfelt, J. H.; Via, G. H.; Lytle, F. W. *J. Chem. Phys.* **1980**, *72*, 4832.
(4) Sinfelt, J. H. *Acc. Chem. Res.* **1987**, *20*, 134.
(5) Sinfelt, J. H. *J. Catal.* **1973**, *29*, 308.
(6) Sinfelt, J. H. *Bimetallic Catalysis: Discoveries and Applications*; Wiley: New York, 1983.
(7) Clarke, J. K. A.; Creaner, A. C. M. *Ind. Eng. Chem. Prod. Res. Dev.* **1981**, *20*, 574.
(8) Meitzner, G.; Via, G. H.; Lytle, F. W.; Fung, S. C.; Sinfelt, J. H. *J. Phys. Chem.* **1988**, *92*, 2925.
(9) Harada, M.; Asakura, K.; Toshima, N. *J. Phys. Chem.* **1993**, *97*, 5103.
(10) Koper, M. T. M. *Surf. Sci.* **2004**, *548*, 1.
(11) Reyes, P.; Figueroa, A.; Pecchi, G.; Fierro, J. L. G. *Catal. Today* **2000**, *62*, 209.
(12) Anderson, J. A.; Fernández-García, M.; Hallerz, G. L. *J. Catal.* **1996**, *164*, 477.
(13) Leon y Leon, C. A.; Vannice, M. A. *Appl. Catal.* **1991**, *69*, 305.
(14) Liu, Y.; Liu, D. *Int. J. Hydrogen Energy* **1999**, *24*, 351.
(15) Saaid, I. M.; Mohamed, A. R.; Bhatia, S. *J. Mol. Catal., A: Chem.* **2002**, *189*, 241.
(16) Yeates, R. C.; Somorjai, G. A. *Surf. Sci.* **1983**, *134*, 729.
(17) Rodriguez, J. A. *Surf. Sci. Rep.* **1996**, *24*, 223.
(18) Kitchin, J. R.; Nørskov, J. K.; Barteau, M. A.; Chen, J. G. *Phys. Rev. Lett.* **2004**, *93*, 156801.
(19) Sachtler, J. W. A.; Somorjai, G. A. *J. Catal.* **1983**, *81*, 77.
(20) Sinfelt, J. H.; Carter, J. L.; Yates, D. J. C. *J. Catal.* **1972**, *24*, 283.
(21) Ponec, V.; Sachtler, W. M. H. *J. Catal.* **1972**, *24*, 250.
(22) González, S.; Sousa, C.; Fernández-García, M.; Bertin, V.; Illas, F. *J. Phys. Chem. B* **2002**, *106*, 7839.
(23) Sousa, C.; Bertin, V.; Illas, F. *J. Phys. Chem. B* **2001**, *105*, 1817.
(24) Gonzalez, S.; Sousa, C.; Illas, F. *Surf. Sci.* **2003**, *531*, 39.
(25) Florez, E.; Tiznado, W.; Mondragón, F.; Fuentealba, P. *J. Phys. Chem. A* **2005**, *109*, 7815.
(26) Jaque, P.; Toro-Labbe, A. *J. Chem. Phys.* **2002**, *117*, 3208.
(27) Jaque, P.; Toro-Labbe, A. *J. Phys. Chem. B.* **2004**, *108*, 2568.
(28) Poater, A.; Duran, M.; Jaque, P.; Toro-Labbe, A.; Solà, M. *J. Phys. Chem. B* **2006**, *110*, 6526.
(29) Hohenberg, P.; Kohn, W. *Phys. Rev.* **1964**, *136*, B864.
(30) Kohn, W.; Sham, L. J. *Phys. Rev.* **1965**, *137*, A1697.
(31) Parr, R. G.; Yang, W. *Density Functional Theory of Atoms and Molecules*; Oxford University Press: New York, 1989.
(32) Chattaraj, P. K.; Liu, G. H.; Parr, R. G. *Chem. Phys. Lett.* **1995**, *237*, 171.
(33) Fuentealba, P.; Pérez, P.; Contreras, R. *J. Chem. Phys.* **2000**, *113*, 2544.
(34) Galván, M.; Dal Pino, J. A.; Joannopoulos, J. D. *Phys. Rev. Lett.* **1993**, *70*, 21.
(35) Mañanes, A.; Duque, F.; Méndez, F.; López, M. J.; Alonso, J. A. *J. Chem. Phys.* **2003**, *119*, 5128.
(36) Parr, R. G.; Szentpály, L. V.; Liu, S. *J. Am. Chem. Soc.* **1999**, *121*, 1922.
(37) Pearson, R. G.; Palke, W. E. *J. Phys. Chem.* **1992**, *96*, 3283.
(38) Parr, R. G.; Pearson, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 7512.
(39) Janak, J. F. *Phys. Rev. B* **1978**, *18*, 7165.
(40) Geerlings, P.; De Proft, F.; Langenaekerm, W. *Chem. Rev.* **2003**, *103*, 1793.
(41) Vargas, R.; Garza, J.; Cedillo, A. *J. Phys. Chem. A* **2005**, *109*, 8880.
(42) Parr, R. G.; Yang, W. *J. Am. Chem. Soc.* **1984**, *106*, 4049.
(43) Senet, P. *J. Chem. Phys.* **1997**, *107*, 2516.
(44) Fuentealba, P.; Contreras, R. In *Reviews in Modern Quantum Chemistry. A Celebration of the Contributions of Robert G. Parr*; Sen, K., Ed.; World Scientific: Singapore, 2003; p 1013.
(45) Tiznado, W.; Chamorro, E.; Contreras, R.; Fuentealba, P. *J. Phys. Chem. A* **2005**, *109*, 3220.
(46) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.
(47) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.
(48) Hay, J. P.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299.
(49) Guvelioglu, G. H.; Ma, P.; He, X.; Forrey, R. C.; Cheng, H. *Phys. Rev. Lett.* **2005**, *94*, 026103.
(50) Derosa, P. A.; Seminario, J. M.; Balbuena, P. B. *J. Phys. Chem. A* **2001**, *105*, 7917.
(51) Efremenko, I.; Sheintuch, M. *Chem. Phys. Lett.* **2005**, *401*, 232.
(52) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision C.02; Gaussian, Inc.: Wallingford, CT, 2004.
(53) Noury, S.; Krokidis, X.; Fuster, F.; Silvi, B. TopMod package; Universite Pierre et Marie Curie, 1997.
(54) Morse, M. D.; Hansen, G. P.; Langridge-Smith, P. R. R.; Zheng, L.-S.; Geusic, M. E.; Michalopoulos, D. L.; Smalley, R. E. *J. Chem. Phys.* **1984**, *80*, 5400.
(55) Kant, A. *J. Chem. Phys.* **1964**, *41*, 1872.
(56) Huberg, K. P.; Herzberg, G. *Molecular Spectra and Molecular Structure-IV*; Van Nostrand Reinhold: New York, 1989.
(57) Rohlfing, E. A.; Valentini, J. J. *J. Chem. Phys.* **1986**, *84*, 6560.
(58) Shim, I.; Gingerich, K. A. *J. Chem. Phys.* **1984**, *80*, 5107.
(59) Yuan, D. W.; Wang, Y.; Zeng, Z. *J. Chem. Phys.* **2005**, *122*, 114310.
(60) Mayer, I. *Chem. Phys. Lett.* **1983**, *97*, 270.
(61) Mineva, T.; Russo, N.; Toscano, M. *Int. J. Quantum Chem.* **2000**, *80*, 105.
(62) Nygren, M. A.; Siegbahn, P. E. M.; Wahlgren, U.; Akeby, H. *J. Phys. Chem.* **1992**, *96*, 3633.