PHYSICAL REVIEW B **73**, 115423 (2006)

Transition-metal atom adsorption on an F_s defect site of MgO (100) and the interaction with a hydrogen atom

Elizabeth Florez,[1] Fanor Mondragón,[1,*] Thanh N. Truong,[2] and Patricio Fuentealba[3]
[1]*Institute of Chemistry, University of Antioquia, A. A. 1226, Medellín, Colombia*
[2]*Henry Eyring Center for Theoretical Chemistry, Department of Chemistry, University of Utah, 315 South 1400 E, Room Dock, Salt Lake City, Utah 84112, USA*
[3]*Department of Physics, University of Chile, Las Palmeras 3425, Ñuñoa, Santiago, Chile*

(Received 11 June 2005; revised manuscript received 14 November 2005; published 24 March 2006)

The interaction of transition metals belonging to the group Pt-Pd-Ni and the period Ni-Cu-Zn, with an F_s center of the MgO (100) surface was investigated using density functional theory. This study was aimed at finding the effect of the electron delocalization of an MgO oxygen vacancy on the interaction energies of the metals with the defect and the electronic configuration of the adsorbed metal atom. The degree of electron delocalization was determined from the maximum values of the electron localization function (ELF). It is confirmed that there are two electrons largely localized in the center of the F_s vacancy. These electrons can delocalize over an adsorbed metal atom. This is the reason for the stabilization of some surface complexes. The MO analysis shows that the filling and the symmetry of the last occupied orbitals of the complex M-F_s/MgO depends on the kind of metal. In the case of Ni and Pt the orbitals from HOMO until HOMO-4 are *d* orbitals and the interaction orbital is the HOMO-5, while for Pd the interaction orbital is the HOMO and the orbitals HOMO-1 until HOMO-5 are *d* character. This information is very useful for the study of the interaction of a hydrogen atom with del metal-F_s/MgO complex. The oxygen vacancy modifies the interaction of a hydrogen atom with a metal deposited on the defect site due to changes in the electronic configuration of the metal. Therefore, the chemical activity of the metal strongly depends on the interaction metal support.

DOI: 10.1103/PhysRevB.73.115423 PACS number(s): 68.35.Md, 68.43.Bc, 68.43.Fg, 82.65.+r

I. INTRODUCTION

The study of the interaction of metal atoms and metal clusters with an oxide surface is of great interest because those systems are widely used in several technological applications, particularly the materials where the interface plays a key role in their physical and chemical properties.[1,2] This reason has made it the focus of many experimental[3,4] and theoretical studies.[5,6] The chemical reactivity of an oxide surface is largely dominated by the presence of point defects such as steps, kinks, foldings, vacancies, etc.[7–9] In particular, the F_s centers have been characterized experimentally.[10,11]

Many studies have centered on the study of metal atoms adsorbed on a defect site, in particular on surface oxygen vacancies.[6,12,13] The theoretical studies have focused on the geometrical structure and electronic characterization of the metal-support interface[12,14] and have studied the effect that these defect sites have on the chemical reactivity of adsorbed metal atoms.[15,16] Pacchioni *et al.*[17] found that Pd atoms deposited on the regular structure of a MgO surface are inert for the acetylene to benzene cyclization. However, when they are bound to a defect site, the metal becomes catalytically active. Different computational approaches have been utilized to study the metal-support interface. For example, Rosch *et al.*[12] studied the electronic properties of deposited transition metals (Ag, Cu, Ni) on oxygen vacancies and regular sites of the MgO (001) surface, analyzing the changes of the dipolar moment and electronic occupation parameters. They found a displacement of the electron density from the vacancy to the adsorbed metal atom. When the defect site has two electrons, F_s center, the shift is larger for Ni and when it has one electron, F_s^+ center, the shift is larger for Ag and Cu.

Recently, topological analysis methods of the electron density such as the atoms-in-molecules (AIM) theory[18] and the electron localization function[19] (ELF) have been used to study the F_s centers of the MgO surface.[20] It has been shown that these topological schemes provide the means to quantify and to characterize the electrons localized in the vacancies of these surfaces. In particular, the ELF topological analysis, which is a tool for characterizing electron (de)localization in the ionic MgO system, is considered more advanced than other population analysis schemes based on orbital-dependent techniques. This methodology was recently applied to study the interaction of Pd atoms on ionic and covalent oxides [i.e., MgO (001), α–Al_2O_3 (0001), and α–SiO_2].[21] However, no attempt was made to investigate the reactivity of these systems.

The goal of this work is to carry out a systematic study of the interaction of transition metals of different electronic configurations with a surface oxygen vacancy of MgO utilizing the ELF as tool to describe the degree of delocalization of the electrons of an F_s center at the interface metal support and to use this information to characterize the chemical reactivity of the metals deposited on it using hydrogen as the probe atom.

II. THEORETICAL BACKGROUND

A brief review of some of the most important points of the topological analysis of the ELF which are relevant to the investigation of electron delocalization are given in this section. For more detailed explanations the reader is referred to an available review.[22]

In 1990, Becke and Edgecombe[19] proposed the electron localization function and in 1994, Silvi and Savin[23] generalized its application using topological tools as was done in the atoms in molecules (AIM) model.[18] The ELF is expressed in terms of the local kinetic energy density excess due to Pauli's repulsion, D, and the Thomas-Fermi's kinetic energy density D_h:[24,25]

$$\eta(r) = \frac{1}{\left(1 + \frac{D}{D_h}\right)^2}. \qquad (1)$$

In the case of monodeterminantal wave functions built in terms of the Hartree-Fock or Kohn-Sham's orbitals[26] $\varphi_i(r)$, D can be interpreted as the difference between the positive definite local kinetic energy of a system of noninteracting fermions $T_s[\rho(r)]$ and the von Weizaecker kinetic energy density $T_w[\rho(r)]$. Therefore, for systems of closed shell:

$$D = t_s[\rho(r)] - t_w[\rho(r)], \qquad (2)$$

$$t_s[\rho(r)] = \frac{1}{2}\sum_{i=1}^{N} |\nabla \varphi_i(r)|^2, \qquad (3)$$

$$t_w[\rho(r)] = \frac{1}{8}\frac{|\boldsymbol{\nabla}\rho(r)|^2}{\rho(r)}, \qquad (4)$$

where the electronic density $\rho(r)$ is calculated in terms of the spin orbitals $\varphi_i(r)$:

$$\rho(r) = \sum_{i=1}^{N} |\varphi_i(r)|^2. \qquad (5)$$

Finally, the Thomas-Fermi's kinetic energy density of homogeneous electron gas, is expressed as

$$D_h = \frac{3}{10}(3\pi^2)^{2/3}\rho(r)^{5/3}. \qquad (6)$$

The values for the ELF, Eq. (1), are found in the interval (0–1). A space region with a high value of the ELF is interpreted as a region where it is more probable to find either an electron or a pair of localized electrons.

The topological analysis of the ELF gradient field yields basins that partition the molecule space conveying the chemical picture of electron pairs, lone or bonded. The integration of the one-electron density $\rho(r)$ and of the pair function $\pi(r_1, r_2)$ over the volume Ω of the basin provides the population $\bar{N}(\Omega)$ of a basin and its variance σ^2. The relative fluctuacion $\lambda = \sigma^2/\bar{N}(\Omega)$ provides an indication of the delocalization within that basin, while the percent contribution fluctuation gives a quitatitative measure of the contributions of other basins to the variance σ^2.[27] λ will be used to describe the degree of the localization, where values above 0.45 denote delocalized electrons.[25]

III. COMPUTATIONAL DETAILS

The defective MgO(100) surface is modeled by an embedded cluster approach. In this approach, a cluster of $Mg_{13}O_{12}$ is selected from the MgO(100) surface to represent an oxygen vacancy where the surface oxygen atom in the center of the above cluster is removed. In the embedded cluster approach, these quantum clusters are surrounded by a set of total ion model potentials (TIMP) for all Mg^{2+} ions that are nearest to any oxygen atom and a set of point charges whose unit cell was within 1.2 nm from any of the quantum cluster atoms. These TIMP and point charges (PC $= \pm 2$) are located at the lattice positions, which were taken from the experimental MgO bulk structure. With these TIMP's, the artificial polarization of oxygen anions at the cluster borders can be reduced.[28,29] The Madelung potential from the remaining extended MgO surface is represented by a set of surface charges derived from the surface charge representation of the external embedded potential (SCREEP) method.[30,31]

Although the formulation of the SCREEP surface has been previously described in full detail,[31] for a complete description of our model a brief overview is given here. First, we draw a closed surface **S** such that all cluster atoms are in the interior of the surface. Then, based on a well-known theorem from electrostatics, no matter what the external charge distribution outside of **S** is, the electrostatic potential inside **S** can be rigorously replaced with some surface charge density ρ located on **S**. In practice, the Ewald summation method is used to calculate the Madelung potential at points on **S** and then substract the contribution from the explicit point charges to yield Φ_{diff} for these points. Due to computational reasons the boundary element method is employed to make **S** discrete. ρ is used as a set of point charges $\mathbf{q}$ that satisfy the matrix equation $Aq = V$. Here the vector $\mathbf{V}$ contains values of Φ_{eff} at points r_j on the surface **S**, and **A** is the $M \times M$ nonsingular matrix with matrix elements:

$$A_{ij} = \frac{1}{|r_i - r_j|} \quad \text{for } i \neq j \text{ and } A_{ii} = 1.07\sqrt{\frac{4\pi}{S_i}}. \qquad (7)$$

Nondiagonal elements A_{ij} represent a generic Coulomb interaction between surface elements r_i and r_j. The diagonal A_{ii} describes the self-interaction of the surface element r_j.

It has been published[32] that in the interaction of Ni, Pd, Pt with a defect center, it is important to account for the correlation energy. Therefore, in this work, the quantum mechanical region was treated by the hybrid B3LYP density functional theory method. In addition the method is slightly dependent on the basis set chosen in the study of these systems.[32] The LANL2DZ[33] pseudopotential with its corresponding basis set was used for transition metal $6\text{-}31G(d,p)$ basis set for Mg and O atoms and $6\text{-}311G(d,p)$ basis set for hydrogen atom were used. In order to improve the performance of the pseudopotential the basis set was augmented with s, p, and d diffuse functions. For the energetic properties, the basis set superposition error corrections using the full counterpoise method of Boy and Bernardi[34] are included. Electronic structure calculations were done using the GAUSSIAN 03 program[35] and the topo-

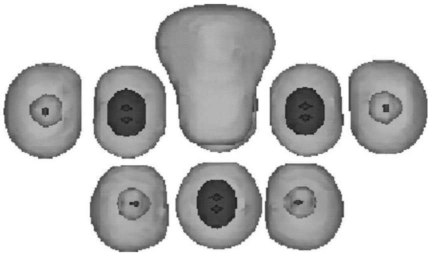

FIG. 1. Schematic representation view of the localization domains of the electron localization function for the ground state of the oxygen vacancy at an isosurface value of $\eta = 0.70$. The electrons of the vacancy are higly located and have a domain that expands beyond the surface of the cluster.

logical analysis of the electron localization function was performed using the TOP-MOD program.[36]

IV. RESULTS AND DISCUSSION

Electronic structure of transition metals adsorbed on an oxygen vacancy. The electronic structure of the F_s center has been extensively studied both theoretically as well as experimentally.[8,9] These centers are formed when a neutral oxygen atom is removed from the oxide surface, leaving behind two electrons which are located in the cavity of the defect. Illas *et al.*,[20] carried out a rigorous characterization of this defect utilizing ELF and AIM approximations. They concluded that this center behaves as a quantum subsystem characterized by a high degree of electronic localization. In this work, the ELF analysis of the F_s center showed that the electronic population of this quantum subsystem is approximately 2 *e*'s, which is in agreement with Illas *et al.*[20] In addition it was determined that the maximum value of the ELF and the relative fluctuation (λ) for this quantum subsystem are 0.99 and 0.39, respectively, suggesting that the electronic density is highly located in this space region.

Figure 1 depicts the electron localization domains for the 0.70 isosurface of the ELF function corresponding to the F_s. It can be observed that the electronic density of the two electrons in the oxygen vacancy is highly localized in the center of the defect cavity and its domain expands out of the MgO cluster surface. The specific electronic arrangement makes this F_s center a likely place for interaction with electrophilic species.

Some authors have found that when a Pd atom is placed on an F_s defect center, there is a delocalization of the vacancy electrons over the metal atom.[13] This effect was investigated by determining the ELF and the relative fluctuation λ values of the interaction of different metal atoms with the electronic density of the vacancy. It is important to keep in mind that the closer the ELF value is to 1.0, the larger the electron localization becomes. Relative fluctuation values below 0.5 also indicate electron localization.

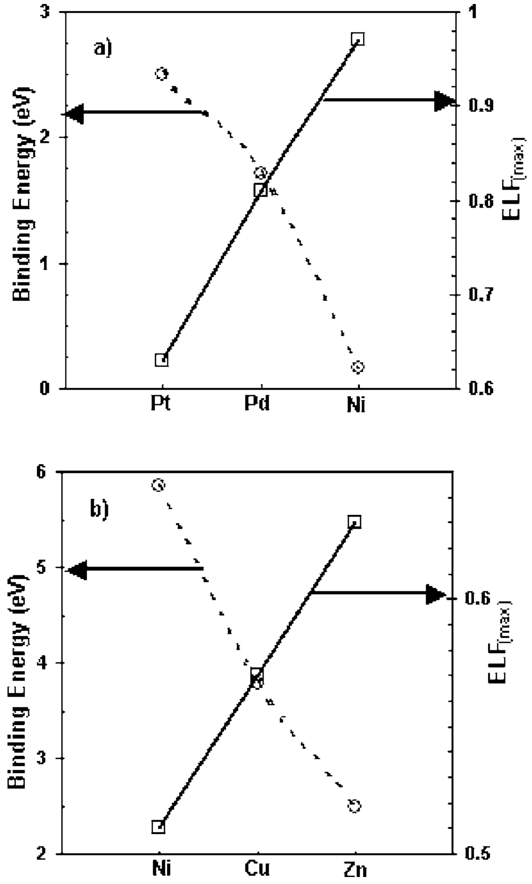

FIG. 2. Comparison of the binding energies and maximum value for the ELF(η) of the defect's basin along (a) group and (b) period.

In Fig. 2(a), the relation among the binding energy and the ELF maximum value for the Ni, Pd, and Pt group are shown. The values of the binding energy and the tendency in this group are in agreement with theoretical data reported for these systems.[13] The tendency of the binding energy is Pt > Pd > Ni and the tendency of the ELF maximum values is the reverse: Ni > Pd > Pt. From these results it can be concluded that the relation between the binding energy and the ELF maximum value is inversely proportional, this means that when the binding energy is large the delocalization of the electrons of the cavity on the metal is also large. The electron delocalization analysis can also be carried out with the aid of the relative fluctuation λ the results of the calculations are shown in Table I. The metal with the strongest interaction has the largest λ value.

In order to investigate the degree of electron delocalization with the metal, the contribution of the metal to the fluctuation of the basin of the interaction was determined. These values are represented in Table I. It can be seen that the percentage of contribution is in the order Pt > Pd > Ni > Cu > Zn, which is exactly the order of the binding energies. The values also present a significant difference between the group

TABLE I. Relative fluctuation (λ) and contribution of the metal basin to the variance ($\sigma 2$) of the defect basin.

	M/F_s				
Parameters	Pt	Pd	Ni	Cu	Zn
Relative fluctuation (λ)	0.91	0.78	0.75	0.61	0.52
Cross contribution (%)	86.5	69.7	67.3	54.5	21.4

Pt, Pd, and Ni with respect to Cu and Zn metal atoms corroborating the fact that the first three metals have stronger interaction with the F_s center.

In Fig. 2(b), the results obtained for the Ni, Cu, and Zn period show that the trend of the binding energies is $\mathrm{Ni} > \mathrm{Cu} > \mathrm{Zn}$ and the trend for the ELF maximum value is $\mathrm{Zn} > \mathrm{Cu} > \mathrm{Ni}$. This is the same relation between these two parameters as the previous one. At the same time, it was found that the Zn ELF value (0.98) is almost the same as the one observed for the F_s center. These results suggest that the two electrons of the vacancy are not taking part in any bonding and therefore the interaction between the Zn metal atom and the vacancy is very weak or nonexistent. As shown in Table I, Cu and Zn are the metals with the lowest λ and at the same time the lowest contribution to the basin formed with the electrons of the defect. These metals will be loosely bound to such a support and therefore can be detached relatively easily from the surface.

In the transition metals group we note that the adsorption of the metal atoms on the F_s center is dominated by a strong interaction between the metal and the vacant site; the level of electron delocalization at the defect center depends on the type of metal, as can be seen in Figs. 3 and 4. From the ELF isosurfaces, it can be seen that the delocalization is larger for the interaction Pt-F_s and the type of interaction for the group of Pt, Pd, and Ni is different than the one of the group of Cu and Zn. As has been observed by other authors, in the case of transition metal atoms, the ELF values are generally below 0.5 which is the limit of the homogeneous electron gas.[37]

In the case of the Pd atom adsorbed on the F_s center, the bonding orbital [highest occupied molecular orbital (HOMO)] of $\mathrm{Pd/F}_s$ (−0.097937 Hartree) is formed by interaction of the empty orbital $5s$ of the Pd and the orbital of the F_s center. It is stabilized by about 1.25 eV relative to the vacancy level, −0.051973 Hartree and this difference in energy can be an explanation of the large value of the binding energy (2.4 eV). On the other hand, the orbitals from HOMO-1 until HOMO-5 are of d character with the following energy sequence $dx-y > dx-z = dy-z > dz^2 > dx^2-y^2$ and their energies in Hartrees are −0.12722, −0.13703, −0.13705, −0.14043, respectively.

For Pt and Ni atoms, the adsorption energies are presented in a somewhat different way. The electronic configurations in their ground states are triplet with a configuration d^9s^1, but when these atoms interact with the F_s defect, there is a repulsion between the electron of the s orbital of the metals and the orbital of the defect which has an s symmetry. This causes the electron found in the s orbital of the metals to be displaced to the d orbital. Therefore, when Ni and Pt are adsorbed on an F_s center, these metals exhibit a closed-shell ground state wich corresponds to an effective d^{10} configuration. The electronic configuration, calculated by analysis of the Natural Bond Orbital theory results of Ni and Pt in the $\mathrm{M/F}_s$ complexes is $4s^{1.41}3d^{9.81}$ and $6s^{1.57}5d^{9.85}$. This analysis is in agreement with previously reported research.[12,38,39]

The energies to change the configuration from triplet to singlet state for the Pt and Ni atoms are 0.51 and 1.52 eV, respectively. The relatively low-energy value for Pt can be an explanation of why the binding energy of this metal is larger than the one in the Ni. On the other hand, the highest occupied orbitals, of the metal-defect complexes, from HOMO to HOMO-4, are the orbitals with an effective d^{10} configuration. For $\mathrm{Pt/F}_s$ the total energies (in Hartrees) are −0.116092, −0.124500, −0.130231=−0.130231, −0.135115 and their configurations are $dx-y$, dz^2, $dx-z=dy-z$, and dx^2-y^2, respectively. For the system $\mathrm{Ni/F}_s$ the energies are −0.066434, −0.067649, −0.070480, and −0.071180=−0.071180 and the configurations are $dx-y$, dz^2, dx^2-y^2, and $dx-z=dy-z$, respectively. The HOMO-5 orbital is the binding orbital in the complexes $\mathrm{Pt/F}_s$ and $\mathrm{Ni/F}_s$. That orbital is formed by the interaction of the metal ns orbital with level of the vacancy. The total energies of the bonding orbital are (in Hartree) −0.138983 for the $\mathrm{Pt/F}_s$ and −0.102165 for the $\mathrm{Ni/F}_s$. On the other hand, comparison of the energy of the Ni and Pt orbitals with d^{10}, with the energy of the vacancy orbital shows that the Ni d^{10} and the vacancy orbital, are at the same energy level, while in the case of the $\mathrm{Pt/F}_s$ the energy is lower. This effect is seen in the larger binding energy of the $\mathrm{Pt/F}_s$ than that of the $\mathrm{Ni/F}_s$. The differences between the HOMO of the metal complexes and the vacancy orbital are 0.20 eV for $\mathrm{Ni/F}_s$ and 1.55 eV for $\mathrm{Pt/F}_s$.

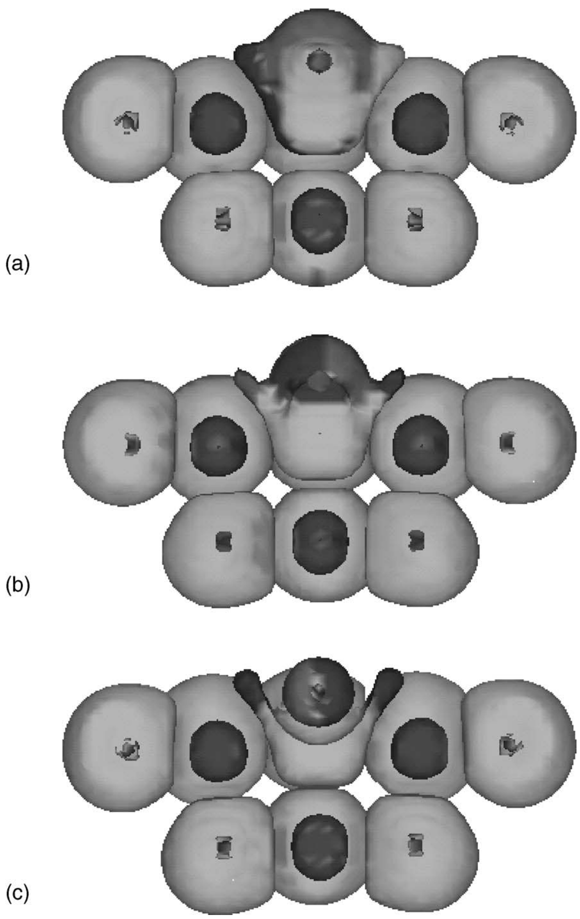

FIG. 3. Schematic representation view of the localization domains of the electron localization function for the ground state of the $\mathrm{M/F}_s$ complexes. (a) $\mathrm{Pt/F}_s$ complex at an isosurface value of $\eta=0.30$. (b) $\mathrm{Pd/F}_s$ complex at an isosurface value of $\eta=0.30$. (c) $\mathrm{Ni/F}_s$ complex at an isosurface value of $\eta=0.30$.

For the Cu and Zn atoms a weak interaction with the oxygen vacancy is observed. This behavior is due to the

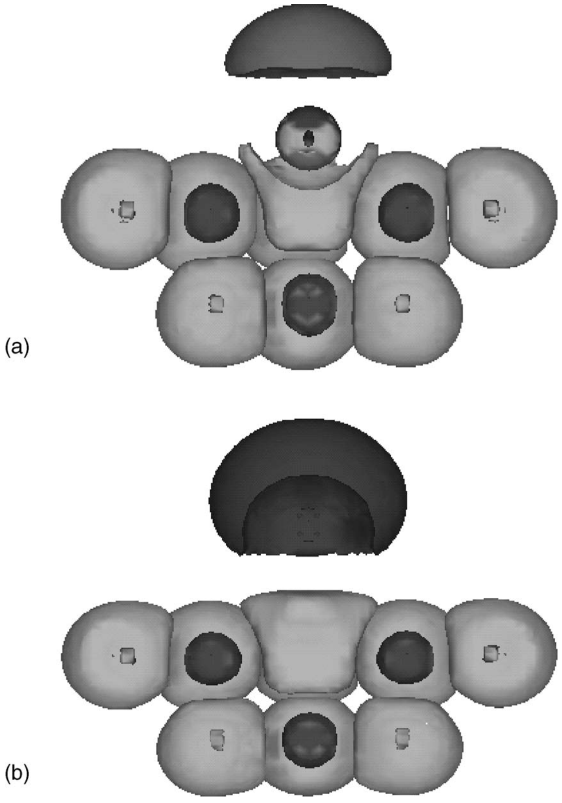

FIG. 4. Schematic representation view of the localization domains of the electron localization function for the ground state of the M/F_s complexes. (a) Cu/F_s complex at an isosurface value of $\eta=0.30$. (b) Zn/F_s complex at an isosurface value of $\eta=0.30$.

stronger Pauli repulsion between the defect site orbital and the s orbital, half full $(Cu:d^{10}s^1)$ or completely full $(Zn:d^{10}s^2)$ being the Zn atom the one with the largest repulsion. In the Cu the HOMO orbital (total energy: −0.02899 Hartrees) is antibonding with one electron provided by the F_s. This HOMO orbital is 0.62 eV higher than the orbital of the F_s center (−0.051973 Hartrees), causing a larger destabilization of the Cu/F_s complex compared to that of the metal complexes where there are no electrons in the antibonding orbital. The bonding orbital is the HOMO-1 (−0.14216 and −0.13226 Hartrees) which has two electrons, one from the 4s orbital and the other from the defect orbital. In the case of the Zn-defect system, there is no apparent interaction at all [see Fig. 4(b)].

Chemical activity of the complex M/F_s in the interaction with a hydrogen atom. The theoretical and experimental study of transition metal hydrides provides useful information for the understanding of metal-hydrogen interactions. Heterogeneous catalysis, using pure metals and supported metals, is one of the areas where these data finds a wide range of application. Therefore, in this research the interaction of a single hydrogen atom with free metal atom and metal atoms supported on an F_s-MgO center was investigated to get an insight into the chemical reactivity of such systems, as well as the effect of the support on the metal reactivity.

In Table II, the interaction energies and electronic configuration of the metal and H atoms of the above described systems are presented. For comparative purposes the results published in the literature for the interaction of atomic hydrogen with free metals are also included. As shown, the data here obtained agrees very well with the results published by different authors.[40–43]

It is important to observe that in the MH systems there is a tendency to an increase of the electronic populations of the 1s orbital of the hydrogen atom, suggesting that in these cases there is a charge transfer from the metal towards the hydrogen atom which follows the trend $Ni > Pd > Pt$, this tendency has been explained by the difference in electron affinity of the metals.[44,45] Ni has the lowest electron affinity and Pt the highest. In the case of PtH system, the electronic population of the 1s orbital remains unchanged. The large electron affinity of Pt has been explained based on relativistic effects as well as on the lanthanide contraction of the s orbital of Pt, increasing in this way its electronegativity. Both of these effects help to explain the reduction of charge transfer from Pt to the H as compared to NiH and PdH.

The hydrogen-metal bond can be formed in two ways. One is due to the interaction of the 1s orbital of the hydrogen atom with the ns orbital of the transition metals. The second one is when the $(n-1)d$ of the transition metal takes part in the bonding. For the CuH system the bonding is only due to the interaction of the H(1s) and Cu(4s) orbitals, there is no contribution of the d orbitals. In the case of Ni, Pd, and Pt hydrides, it is observed that in the MH bonding there is an important contribution of the d orbitals. For this group, the H adsorption energy has been related to the $(n-1)d$ orbitals.[44,45] The energy of the bonding increases in the sequence $Ni < Pd < Pt$ (MH binding energy, relative to the triplet state) which is the same order of participation of the d orbitals in the bonding. For Ni, this contribution is almost negligible.

As shown in Table II, the energy of the bonding PdH is weaker than that of the ground state of the singlet Pd, due to a promotion energy to the variation of the configuration d^{10} to s^1d^9.[46] The data in Table II shows that the support can have a strong influence on the metals supported on it. In general, the presence of an oxygen vacancy modifies the interaction of the hydrogen atom with the metals deposited on the defect due to the change of the electronic configuration of the transition metals. For the metals, the configuration is close to $ns^2(n-1)d^{10}$.

In the case of the hydrides $(M/F_s)-H$, a considerable increase in the electronic population of the 1s orbital of the hydrogen atom is observed. The largest increase is for the $(Cu/F_s)-H$ and $(Ni/F_s)-H$ systems with 69 and 62 % increase, respectively. This behavoir can be explained based on the lower value of the gap [HOMO-lowest unoccupied molecular orbital (LUMO)], 0.49 and 1.45 eV for Cu and Ni, respectively. The interaction of the Cu/F_s complex with the H atom is due to the formation of bonding and antibonding linkages by the combination of the single antibonding orbital of Cu/F_s and the s orbital of the H.

In the complex $(Ni/F_s)-H$, the Ni atom has an effective configuration s^1d^9, where the $(n-1)d$ orbital with one electron corresponds to the dz^2 orbital. This suggests that the charge that is transferred to the H atom is from the Ni sup-

TABLE II. Adsorption energies, in eV, of hydrogen atom on free metals and on metals adsorbed on an F_s center of the MgO(100) surface. Electronic configuration of the metal and the H atom in such systems and the gap (HOMO-LUMO) of the M/F_s complexes.

	Systems			
	Pt	Pd	Ni	Cu
Free metal				
E_B, M-H, eV				
This work	$3.52(^2\Sigma_g)$	3.32[a] $(^2\Sigma_g)$ 2.43[b]	$2.89(^2\Sigma_g)$	$2.81(^1\Sigma_g)$
Other source	3.44[c]	2.19[d]	2.92[e]	2.66[f]
Electronic configuration				
Metal	$s^{1.28}d^{8.71}$	$s^{0.45}d^{9.41}$	$s^{0.56}d^{9.08}$	$s^{0.76}d^{9.99}$
Hydrogen atom	$s^{1.0}$	$s^{1.13}$	$s^{1.36}$	$s^{1.33}$
Complex metal vacancy				
E_B, (M/Fs_s)-H, eV	1.89	1.61	2.68	3.09
Electronic configuration				
Metal	$s^{1.45}d^{9.63}p^{0.14}$	$s^{1.25}d^{9.72}p^{0.14}$	$s^{1.22}d^{9.07}p^{0.20}$	$s^{1.27}d^{9.93}p^{0.20}$
Hydrogen atom	$s^{1.23}$	$s^{1.29}$	$s^{1.62}$	$s^{1.69}$
Gap (HOMO-LUMO)	2.64	2.23	1.45	0.49

[a] Relative to the triplet state.
[b] Relative to ground state (singlet).
[c] From Ref. 40.
[d] From Ref. 41.
[e] From Ref. 42.
[f] From Ref. 43.

ported which leads to a very strong Ni^+H^- ionic interaction. In the case of Pt and Pd the variation of the population of the *ns* and $(n-1)d$ is not very significant. It was observed that this bond is formed by the interaction of the electrons of the *ns* and $(n-1)d$ of the metals with the *s* orbital of the hydrogen atom. Due to the strong interaction of the electrons in the *ns* orbital of the metal with those of the F_s center, their interaction with the H atom is not as strong and therefore the contribution of the $(n-1)d$ orbitals becomes more important. The bonding energy of the H on the Pt/F_s is larger than that on the Pd/F due to the higher contribution of the $(n-1)d$ to the bond. This is in agreement with the hybridization of these atoms, Pt $s^{56\%}d^{44\%}$ and Pd $s^{76\%}d^{22\%}$.

It can be observed that the interaction of a hydrogen atom with the Pt/F_s system becomes 1.6 eV weaker due to the effect of the vacancy on the metal, while the interaction with Cu/F_s is the strongest (3.1 eV). The same effect has been found in the nucleation of Pt and Cu.[39,47] Therefore, due to the very strong interaction of the metal with the F_s center, there is a significant change in the electronic structure of the adsorbed Pt atom which consequently affects its reactivity towards hydrogen or other metal atom. This effect is contrary to what happens in the case of Cu where it has been found that the Fs centers are good active sites for nucleation.

V. CONCLUDING REMARKS

Electron localization in the defect site as well as the electron delocalization when an atom is adsorbed on an F_s vacancy was observed. This information is useful to explain the binding energy of a metal on the F_s center. A large electron delocalization implies reduced interaction of the metals with the adsorbed hydrogen atoms. A clear tendency can be obtained from the difference HOMO-LUMO which correlates very well with the energy of the bonding of a hydrogen atom to the metals supported on the F_s center of MgO. Pt has the strongest interaction with the oxygen vacancy and is therefore the one which shows the weakest hydrogen adsorption. Although these observations are for the adsorption of atomic hydrogen on one metal atom, it is important that they be considered in the analysis of the support used in different hydrogenation catalysts.

ACKNOWLEDGMENTS

This work was supported by the Sostenibilidad-2005 Program of the University of Antioquia. Part of this work has been supported through the Millennium Nucleus for Applied Quantum Mechanics and Computational Chemistry, Project No. P02-004-F and Fondecyt Grant No. 1050294. E.F. would like to thank Colciencias and the University of Antioquia for her Ph.D. scholarship.

*Electronic address: fmondra@quimbaya.udea.edu.co

[1] V. E. Henrich and P. A. Cox, *The Surface Science of Metal Oxides* (Cambridge University Press, Cambridge, 1994).

[2] *Chemisorption and Reactivity on Supported Clusters and Thin Films*, edited by R. M. Lambert and G. Pacchioni, Vol. 331 of *NATO ASI Series E: Appl. Sci.* (Plenum, New York, 1997).

[3] G. Renaud, O. Robach, and A. Barbier, Faraday Discuss. **114**, 157 (1999).

[4] C. R. Henry, Surf. Sci. Rep. **31**, 231 (1998).

[5] A. Markovits, J. C. Paniagua, N. Lopez, C. Minot, and F. Illas, Phys. Rev. B **67**, 115417 (2003).

[6] A. M. Ferrari and G. Pacchioni, J. Phys. Chem. **100**, 9032 (1996).

[7] M. C. Wu, C. M. Truong, K. Coulter, and D. W. Goodman, J. Am. Chem. Soc. **114**, 7565 (1992).

[8] A. M. Ferrari and G. Pacchioni, J. Phys. Chem. **99**, 17010 (1995).

[9] Y. D. Kim, J. Stultz, and D. W. Goodman, Langmuir **18**, 3999 (2002).

[10] C. Barth and C. R. Henry, Phys. Rev. Lett. **91**, 196102 (2003).

[11] M. Sterrer, E. Fischbach, T. Risse, and H. J. Freund, Phys. Rev. Lett. **94**, 186101 (2005).

[12] A. V. Matveev, K. M. Neyman, I. V. Yudanov, and N. Rosch, Surf. Sci. **426**, 123 (1999).

[13] C. DiValentin, L. Giordano, G. Pacchioni, and N. Rosch, Surf. Sci. **522**, 175 (2003).

[14] N. Lopez, J. C. Paniagua, and F. Illas, J. Chem. Phys. **117**, 9445 (2002).

[15] K. Judai, S. Abbet, A. S. Woerz, U. Heiz, L. Giordano, and G. Pacchioni, J. Phys. Chem. B **107**, 9377 (2003).

[16] S. Abbet, E. Riedo, H. Brune, U. Heiz, A. M. Ferrari, L. Giordano, and G. Pacchioni, J. Am. Chem. Soc. **123**, 6172 (2001).

[17] A. M. Ferrari, L. Giordano, G. Pacchioni, S. Abbet, and U. Heiz, J. Phys. Chem. B **106**, 3173 (2002).

[18] R. F. W. Bader, Chem. Rev. (Washington, D.C.) **91**, 893 (1991).

[19] A. D. Becke and K. E. Edgecombe, J. Chem. Phys. **92**, 5397 (1990).

[20] P. Mori-Sánchez, J. M. Recio, B. Silvi, C. Sousa, A. Martín Pendás, V. Luaña, and F. Illas, Phys. Rev. B **66**, 075103 (2002).

[21] J. R. B. Gomes, F. Illas, and B. Silvi, Chem. Phys. Lett. **388**, 132 (2004).

[22] A. Savin, R. Nesper, S. Wengert, and T. F. Fasler, Angew. Chem., Int. Ed. Engl. **36**, 1808 (1997).

[23] A. Savin and B. Silvi, Nature (London) **371**, 683 (1994).

[24] A. Savin, A. D. Becke, J. Flad, R. Nesper, H. Preuss, and H. G. V. Schnering, Angew. Chem., Int. Ed. Engl. **30**, 409 (1991).

[25] A. Savin, B. Silvi, and F. Colonna, Can. J. Chem. **74**, 1088 (1996).

[26] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).

[27] S. Noury, F. Colonna, A. Savin, and B. Silvi, J. Mol. Struct. **540**, 59 (1998).

[28] N. W. Winter and R. M. Pitzer, J. Chem. Phys. **89**, 446 (1988).

[29] V. A. Nasluzov, V. V. Rivanenkov, A. B. Gordienk, K. M. Neyman, U. Birkenheuer, and N. Rosch, J. Chem. Phys. **115**, 8157 (2001).

[30] E. V. Stefanovich and T. N. Truong, J. Chem. Phys. **104**, 2946 (1996).

[31] E. V. Stefanovich and T. N. Truong, J. Phys. Chem. B **102**, 3018 (1998).

[32] N. Lopez and F. Illas, J. Phys. Chem. B **102**, 1430 (1998).

[33] J. P. Hay and W. R. Wadt, J. Chem. Phys. **82**, 299 (1985).

[34] S. F. Boys and F. Bernardi, Mol. Phys. **19**, 553 (1970).

[35] G. W. T. M. J. Frisch, H. B. Schlegel, G. E. Scuseria, J. R. C. M. A. Robb, J. A. Montgomery, Jr., T. Vreven, J. C. B. K. N. Kudin, J. M. Millam, S. S. Iyengar, J. Tomasi, B. M. V. Barone, M. Cossi, G. Scalmani, N. Rega, H. N. G. A. Petersson, M. Hada, M. Ehara, K. Toyota, J. H. R. Fukuda, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, M. K. H. Nakai, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, J. J. C. Adamo, R. Gomperts, R. E. Stratmann, O. Yazyev, R. C. A. J. Austin, C. Pomelli, J. W. Ochterski, P. Y. Ayala, G. A. V. K. Morokuma, P. Salvador, J. J. Dannenberg, S. D. V. G. Zakrzewski, A. D. Daniels, M. C. Strain, D. K. M. O. Farkas, A. D. Rabuck, K. Raghavachari, J. V. O. J. B. Foresman, Q. Cui, A. G. Baboul, S. Clifford, B. B. S. J. Cioslowski, G. Liu, A. Liashenko, P. Piskorz, R. L. M. I. Komaromi, D. J. Fox, T. Keith, M. A. Al-Laham, A. N. C. Y. Peng, M. Challacombe, P. M. W. Gill, W. C. B. Johnson, M. W. Wong, C. Gonzalez, and J. A. Pople, I. Gaussian, GAUSSIAN 03 Wallingford, CT, 2004.

[36] S. Noury, X. Krokidis, F. Fuster, and A. Silvi, TOP-MOD package, University P. M. Curie, Paris, 1997.

[37] J. Poater, M. Duran, M. Sola, and B. Silvi, Chem. Rev. (to be published).

[38] Y. Wang, E. Florez, F. Mondragon, and T. N. Truong, Surf. Sci. (to be published).

[39] A. Bogicevic and D. R. Jennison, Surf. Sci. **437**, L741 (1999).

[40] K. Balasubramanian and P. Y. Feng, J. Chem. Phys. **92**, 541 (1990).

[41] K. Balasubramanian, P. Y. Feng, and M. Z. Liao, J. Chem. Phys. **87**, 3981 (1987).

[42] C. Ashman, S. N. Khanna, and M. R. Pederson, Chem. Phys. Lett. **368**, 257 (2003).

[43] N. B. Balabanov and K. A. Peterson, J. Chem. Phys. **123**, 064107 (2005).

[44] S. W. Wang and K. S. Pitzer, J. Chem. Phys. **79**, 3851 (1983).

[45] P. S. Bagus and C. Bjorkman, Phys. Rev. A **23**, 461 (1981).

[46] C. McM. Rohlfing, P. J. Hay, and R. L. Martin, J. Chem. Phys. **85**, 1447 (1986).

[47] A. del Vitto, C. Sousa, F. Illas, and G. Pacchioni, J. Chem. Phys. **121**, 7427 (2004).