Atomic Sulfur and Chlorine Interaction with Pd_n Clusters ($n = 1-6$): A Density Functional Study

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Sulfur and chlorine change the activity and selectivity of palladium-based hydrogenation catalysts, but the origins of these effects at the microscopic level remain elusive. The chemisorption of atomic sulfur and chlorine on small palladium clusters has been studied with the hybrid Hartree−Fock/density functional method (B3LYP functional). Full geometry optimizations have been performed, allowing the occurrence of low-symmetry structures, in order to investigate the size dependence of atomic adsorption geometry and energy. The latter properties vary in a monotonous way as the number of palladium atoms increase and seem to rapidly converge toward limiting values. Sulfur was found to adsorb on the higher coordination sites, with a Pd−S bond distance of 2.3 Å, whereas chlorine prefers the 2-fold sites and the Pd−Cl bond is longer (2.5 Å). An adsorption energy of about 25−30 kcal/mol per Pd−X bond was estimated for both atoms. The topological analysis of the electron localization function (ELF) revealed that the bond between sulfur or chlorine adatoms and palladium is not of the shared-electrons type.

1. Introduction

Transition metals are important as catalysts in many chemical reactions. They are often used in a dispersed form on oxide supports such as γ-Al_2O_3, SiO_2, or zeolites, and the particle sizes can be rather small (a few hundreds, a few tens of atoms, or even less). The catalytic activity of these small particles is influenced by the nature of the support and by the chemical species present in the reaction medium. In particular, sulfur compounds present in natural sources of hydrocarbons are well-known to act as poisons or inhibitors of the catalyst activity. The toxicity of sulfur would be related to its ability to form strong bonds with the catalyst surface.[1] Extensive research has been done on sulfur poisoning of metallic catalysts.[1−5] The geometric effects are not sufficient to explain the poisoning activity of sulfur compounds, and the electronic properties of metallic particles are thought to play a fundamental role at the thiotolerance level.[5] On the other hand, chlorine compounds are known to give some degree of resistance to sulfur poisoning when added to supported catalysts.[3,5] Their effect would be ascribed to the modification of the metal electronic properties and to a weakening of the metal−sulfur bond. It was shown[3,6] that chlorine inhibits the adsorption of sulfur compounds on alumina support and affects its acidity. In practice the thiotolerance of supported noble metal based catalysts can be obtained by addition of chlorine compounds either at one step of preparation or in the feedstock. In all cases, heating of the catalyst under hydrogen pressure will result in the production of hydrogen chloride, which can be detected in the reactor effluents. The presence of hydrogen chloride in the reaction medium under reducing conditions will result with a high probability in its dissociative chemisorption at the surface of metal particles, besides its well-known reaction with the oxide supports. To our knowledge, no direct proof of the presence of chlorine adatoms or chlorine ions on the metal particles of the working catalyst has been given, although indirect evidence for this was recently obtained.[7] In this paper we took the direct interaction of chlorine with metal surfaces, concurrently with the direct interaction of sulfur, as a working hypothesis for understanding the thiotolerance effect. The rather large binding energies for both adatoms with Pd_n we obtained and report further provide some more a posteriori support for this hypothesis.

To investigate the effect of sulfur and other elemental compounds on palladium catalysts, we started a density functional study on small clusters.[8] In almost all quantum chemical calculations the clusters are selected as rigid pieces of the infinite perfect crystal. The principal features of our approach are the full optimization of the geometry, even in bare metallic clusters, and the choice of the Becke three-parameter functional[9] within the density functional theory framework. This functional, characterized by a mixing of exact exchange ("Hartree−Fock") and exchange−correlation from DFT, has been demonstrated to give better results than standard local or gradient-corrected functionals, for compounds ranging from organics[10,11] to water molecule clusters,[12] transition metal complexes,[13,14] and metal clusters.[8]

With the full optimization approach on small clusters, we hope to get closer to the properties of the bigger particles present in real supported catalysts (neglecting as a first approximation the support effects), as well as the local deformation of a metal surface due to the interaction with the adsorbates. We are thinking that small geometry-optimized clusters probably represent better the lowest coordination sites, such as corner and edge sites, that would be preferred for sulfur adsorption on single-crystal surfaces as well on small metallic particles. This can be expected particularly for metallic systems involving "soft" noble metals, which exhibit weak and nondirectional metal−metal bonds and are therefore much prone to surface reconstruction and possess a high ionic mobility. By contrast, we would expect clusters with fixed or constrained geometries to model much more closely the surface sites of covalent or ionocovalent solids such as silicates or zeolites.[15]

The size dependence of metal cluster properties is also expected to converge much more easily thanks to the full relaxation of the structural parameters and provided that a proper description of the ground spin state is given.[16,17]

In this paper we give an account of our results concerning sulfur and chlorine atom interaction with Pd_n ($n = 1, 2, 3, 4,$

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and 6). Chlorine compounds indeed are important additives, for which it is desirable to better understand the localization and activity. The Pd_nX (X = S, Cl) systems were analyzed from the geometrical, energetic, and electronic points of view. The nature of the chemical bonds was also investigated through the topological analysis of the electron localization function, ELF.[18,19]

2. Computational Details

The calculations reported here were all carried out using the B3LYP density functional option of Gaussian94.[20] This code offers a wide variety of DFT models, LSDA and GGA, as well as hybrid methods,[9,21] which are characterized by a mixing of exact exchange ("Hartree–Fock") and exchange–correlation from DFT. The straightforward substitution of DFT approximate exchange by exact HF exchange has proven to be inadequate for molecules.[22] To consider the exact exchange information, Becke has proposed a hybrid method[21] with a new partitioning of exchange and correlation energies between HF and DFT terms. This partitioning is based on an approximation of the rigorous "adiabatic connection" formula, for the exchange–correlation energy in the Kohn–Sham theory. The following functional was defined and parametrized by Becke:[9]

$$E_{XC} = E_{XC}^{LSDA} + a_0(E_X^{exact} - E_X^{LSDA}) + a_X\Delta E_X^{B88} + a_C\Delta E_C^{PW91} \tag{1}$$

where $a_0 = 0.20$, $a_X = 0.72$, $a_C = 0.81$, E_X^{exact} is the exact exchange energy, ΔE_X^{B88} is Becke's gradient correction for exchange,[23] and ΔE_C^{PW91} is the gradient correction for correlation of Perdew and Wang.[24] The B3LYP functional is built using the Becke gradient correction for exchange[23] and the Lee–Yang–Parr (LYP) correlation functional.[25]

To incorporate the scalar relativistic effects in the calculations, we have used the LanL2DZ[20] basis set (Hay and Wadt relativistic effect core potentials (RECP), small core[26] plus DZ), whereas the standard 6-311G(d,p) basis set[27] was employed for sulfur and chlorine.

The geometry optimizations were performed allowing for low-symmetry groups to occur. In Figures 1 and 2 are ascribed the symmetries that we have determined for the different structures. For $n = 2$, 3, and 4 the possibility of lower (C_1) symmetry was also investigated, whereas the C_s group was fixed for $n = 6$.

3. Results and Discussions

3.1. Interaction of Atomic Sulfur and Chlorine with Pd_n: Adsorption Structures and Energies. The Pd_nX geometries ($n = 1-6$, X = S, Cl) were fully optimized and the Pd_n-X adsorption energies were computed using the results obtained for the bare metallic clusters from a previous work.[8]

In small clusters, the changes in cluster sizes may have significant effects on interaction energies as well as adsorption properties. Thanks to the high accuracy of our calculations, taking account of electronic correlation, full relaxation of structural parameters, and correct spin ground states, we expect to minimize these size effects, or at least to cancel those spurious due to the method.

The average bond lengths and Pd–Pd per-bond energies (PBE) for bare Pd_n clusters are shown in Figures 3 and 4, respectively, and compared with bulk experimental values. Both properties are quickly approaching the bulk limit, showing a monotonous trend.

The Pd_nS structures are displayed in Figure 1. The sulfur atom clearly prefers the 3-fold coordination sites. This is in agreement with the results obtained for adatoms like H, O, and N[16,29,30] and with the back-donative characteristic of the bond, due to the low energy of the atomic LUMO.[16] The Pd–S bond distances converge rapidly to a value of about 2.30 Å, close to the average value of 2.34 Å for the bulk PdS.[31] It moreover falls between the distances obtained from LEED spectroscopy[32,33] for sulfur chemisorption on the Pd(111) surface (3-fold, 2.22 ± 0.03 Å) and on Pd(100) (4-fold, 2.35 ± 0.03 Å). The interaction between S and palladium clusters leads to a significant weakening (lengthening) of the Pd–Pd bonds near the sulfur, especially for Pd_4 and Pd_6.

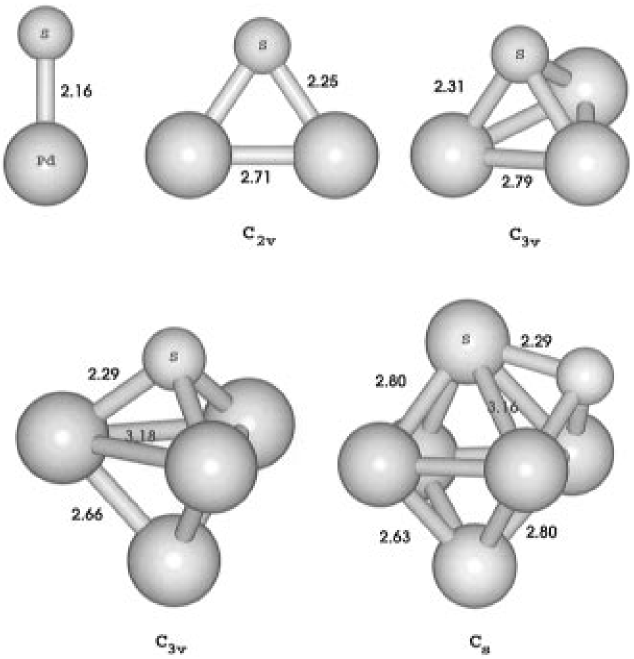

Figure 1. Fully optimized structures for Pd_nS clusters. Numbers denote bond lengths (Å). These pictures have been prepared using MOLDEN.[28]

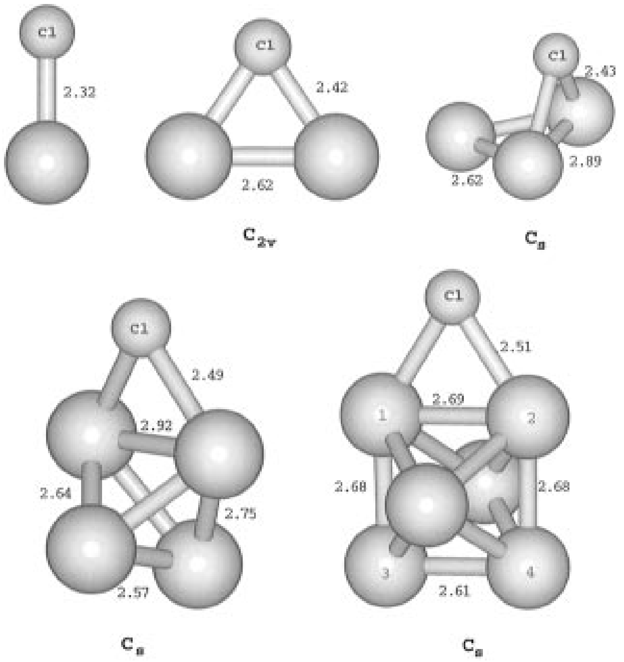

Figure 2. Fully optimized structures for Pd_nCl clusters. Numbers denote bond lengths (Å). For the eight Pd–Pd distances not noted on the Pd_6Cl structure, the four involving atoms 1 and 2 are about 2.79 Å and those involving atoms 3 and 4 are about 2.73 Å. These pictures have been prepared using MOLDEN.[28]

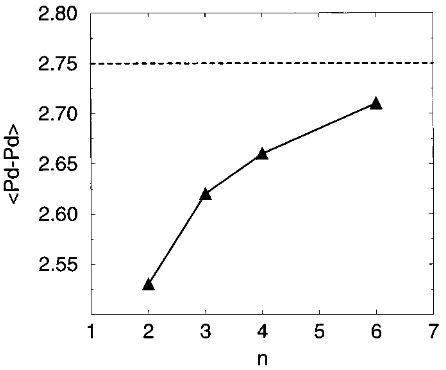

Figure 3. Averaged Pd−Pd bond distances (Å) in the bare Pd$_n$ clusters as a function of the number *n* of palladium atoms. The dashed line denotes the experimental bulk value.

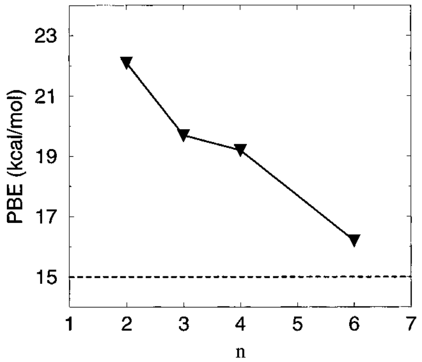

Figure 4. Pd−Pd per-bond energies (PBE) for the bare Pd$_n$ clusters as a function of the number *n* of palladium atoms. PBE is obtained by dividing the atomization energy by the number of Pd−Pd bonds in the cluster. The dashed line denotes the bulk value.

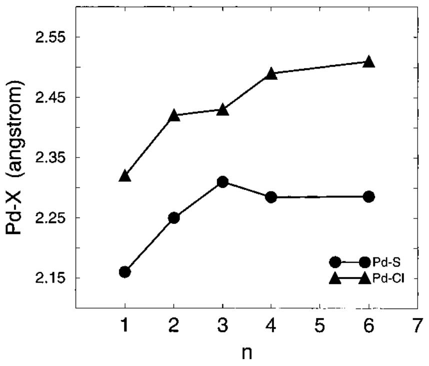

Figure 5. Pd−X (X = S, Cl) bond distances (Å) in the Pd$_n$X clusters as a function of the number *n* of palladium atoms.

The chlorine atom was found to prefer 2-fold coordination (Figure 2). The Pd−Cl bond distances seem to converge to a value of about 2.50 Å, significantly longer than the Pd−S bond. The weakening of Pd−Pd bonds is still present but less important with respect to the sulfur case. This would indicate a lower surface relaxation and reconstruction caused by chlorine with respect to sulfur. For the Pd$_6$Cl cluster, unlike Pd$_6$S, the lengthening of the Pd−Pd bond between metal atoms directly involved with the chlorine chemisorption is smaller than for Pd$_3$Cl and Pd$_4$Cl clusters. The *n* dependence of Pd−X bond lengths is displayed in Figure 5.

The adsorption energies of S and Cl on the Pd$_n$ clusters were computed via eq 2 and are summarized in Table 1.

$$\Delta E_{\mathrm{ads}} = E_{\mathrm{Pd}_n\mathrm{X}} - E_{\mathrm{Pd}_n} - E_{\mathrm{X}} \tag{2}$$

Some tests were done to evaluate the counterpoise corrections for the basis-set superposition error and proved that these corrections are negligible in our calculations (less than 2% of the adsorption energy).

TABLE 1: Total Energies (hartrees) for Pd$_n$, Pd$_n$S, and Pd$_n$Cl and Adsorption Energies (kcal/mol) for S and Cl Calculated Using Eq 2[a]

n	*E*[Pd$_n$]	*E*[Pd$_n$S]	*E*[Pd$_n$Cl]	Δ*E*$_{\mathrm{ads}}$[S]	Δ*E*$_{\mathrm{ads}}$[Cl]
1	−126.7068	−524.9307	−586.9708	−57.7	−61.4
2	−253.4488	−651.7203	−713.7386	−87.5	−77.6
3	−380.2144	−778.5067	−840.4953	−100.6	−72.0
4	−507.0102	−905.2782	−967.2662	−85.3	−56.4
6	−760.5516	−1158.8134	−1220.8216	−81.4	−65.2

[a] The total energies for atomic sulfur and chlorine are respectively −398.132 08 and −460.166 16 hartrees.

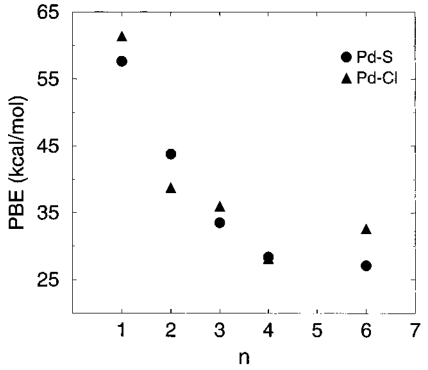

Figure 6. Pd−X (X = S, Cl) per-bond energies (PBE) for the Pd$_n$X clusters as a function of the number *n* of palladium atoms. These values are obtained by dividing the Δ*E*$_{\mathrm{ads}}$ by the number of direct Pd−X bonds.

TABLE 2: Results for Different Symmetries and Multiplicities of Pd$_4$Cl

sym.	mult.	*S*(*S* + 1)	⟨*S*^{2}⟩	*E* (hartrees)
C_1	2	0.75	1.48	−967.2697
C_{2v}	2	0.75	0.77	−967.2637
C_s	4	3.75	3.77	−967.2662

The calculated sulfur adsorption energies are in good agreement with the experimental values estimated from adsorption−desorption isotherms by Oudar and co-workers[2,34] for some transition metal surfaces and range from 78 to 116 kcal/mol (Pt falls in between this interval, and the same is expected for Pd).

Our results demonstrate that sulfur binds more strongly on the palladium clusters than chlorine. Nevertheless, the per-bond energies computed dividing the Δ*E*$_{\mathrm{ads}}$ by the number of Pd−X direct bonds are quite similar and once more seem to quickly converge toward a constant limiting value (Figure 6). The PBE values actually always decrease with increasing *n*. Pd$_6$Cl represents an exception, but it is still close to the apparent asymptotic value, which would be for both Cl and S about 25−30 kcal/mol.

3.2. Electronic and Bond Properties. As for the bare palladium clusters, all the Pd$_n$S clusters were found to have triplet ground states. The Pd$_n$S systems have doublet ground states for *n* = 1−3. In the unrestricted lower energy doublet state found for Pd$_4$Cl the spin contamination was very high. Some results with different symmetry and multiplicity are shown in Table 2. The symmetry constrained (C_{2v}) solution with multiplicity equal to 2 has a higher energy than the quartet state. The low-symmetry doublet solution has the lowest total energy but a very high spin contamination, so, given the small energy differences, this solution was discarded and the quartet was taken to represent the ground state of Pd$_4$Cl. Following D. J. Fox,[35] suggestions, we have done some calculations with the standard

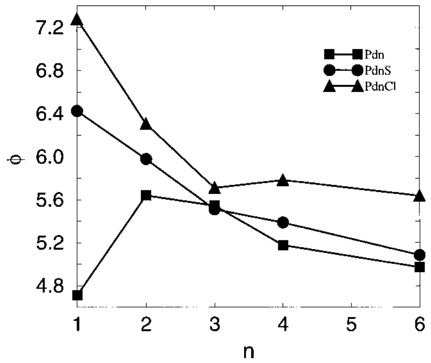

Figure 7. Work function ϕ (eV), estimated using eq 3, for Pd$_n$ clusters isolated or in interaction with S or Cl.

BLYP functional. The same energetics and spin contamination were obtained. This would indicate that the spin contamination does not come exclusively from the Hartree−Fock exchange in the B3LYP functional.

A quartet lower energy state was also found for Pd$_6$Cl. This cluster was studied in the C_s symmetry, with the mirror plane going through Cl and perpendicular to the Pd−Cl−Pd bond triangle. The same constraint was applied for Pd$_6$S, to reduce the computational efforts.

The atom chemisorption properties are very different with respect to those of molecules. The LUMO of an atom has a significantly lower energy than that of a molecule, and the back-donative interaction dominates the binding of adatoms to metal surfaces.[16] The LUMOs obtained for sulfur and chlorine (−5 and −6.9 eV, respectively) are even lower in energy than the Pd$_n$ HOMO (∼ −5 eV). The back-donation leads to a charge transfer from the metal to the adsorbed sulfur or chlorine atom. The net Mulliken atomic charge was found higher for Cl (∼0.30*e*) than for S (∼0.15*e*), due to the lower Cl LUMO and in agreement with the higher electronegativity of chlorine. The atomic orbitals involved in the chemisorption are the Pd d and the S and Cl p.

The ionization potentials (IPs) of small clusters differ from the infinite metal work function and could be significantly size dependent.[36] The experimental IP of the atomic palladium is 8.34 eV (our B3LYP result is 8.6 eV), whereas the bulk palladium work function is 5.1 eV,[37] and the IPs for small metal particles will certainly fall between these two values.

A calculation of IPs from the differences between optimized neutral and charged clusters is computationally expensive for many-atom systems. Russier et al.[38] have shown that it is possible within the density functional theory to link the Fermi energy ϵ_F (or the HOMO energy) of small clusters to the metal work function ϕ. In the case of a spin-polarized system, they defined

$$\phi = -\overline{\epsilon_F} = -\frac{1}{2}(\epsilon_F^{\uparrow} + \epsilon_F^{\downarrow}) \qquad (3)$$

According to Russier et al. only a weak size dependence is expected for ϕ, and the determination of ϕ for modified metallic clusters, e.g. after the chemisorption of some species, should give us information such as $\Delta\phi$, connected to the direction and extent of charge transfer between metal and adsorbates, independently of the size of the cluster. In Figure 7 the work functions calculated using eq 3 for all the systems we have investigated are displayed. Excluding the $n = 1$ case, where there is no metallic bond, the calculated ϕ values seem indeed weakly dependent on the cluster size. For the bare clusters there is a rapid stabilization to a value close to the experimental work function. The effect of adatoms on the Pd clusters is to increase ϕ. The work function variation induced by chlorine is greater than that by sulfur, as should be expected from its greater electronegatively.

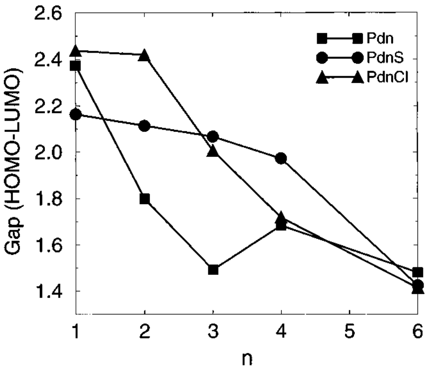

Figure 8. HOMO−LUMO gap (eV) for Pd$_n$ clusters isolated or in interaction with S or Cl.

The HOMO−LUMO gap as a function of *n* (Figure 8) shows a clear tendency to decrease toward the zero value expected for a metallic compound. The effect of one Cl or S adatom on the gap vanishes as the number of metal atoms increases.

3.2.1. Topological Analysis of the Electron Localization Function. The topological analysis of electronic density[39] or alternative functions[18,19,40] provides an interesting tool to overcome the complexity of molecular orbital analysis due to their delocalized character. In this context Becke and Edgecombe[18] introduced an “electron localization function” (ELF) related to the Pauli exclusion principle, which depends on total electronic density, its gradient, and the kinetic energy density. Silvi and Savin[19] have recently shown that the topological analysis of ELF provides a partitioning of the molecular space into attractor basins, which allow for a classification of the chemical bond in molecules and crystals. The attractors are localized through the analysis of the ELF gradient field. There are two types of attractors: core and valence (bonding or nonbonding) attractors. The number of cores connected to a given valence attractor determines its synaptic order.[41] Bonding attractors are di- or polysynaptics, whereas nonbonding are monosynaptics.

An efficient visualization tool has been implemented by Silvi and Savin through the introduction of localization domains bounded by isosurfaces of ELF and containing one (irreducible domain) or more (reducible) attractors. Different color codes are associated with the type of attractors, providing an explicit picture of the bonding.

We have reported in Figure 9 some of these pictures that we have obtained for our systems. The use of small core ECPs allowed us to perform the following analysis of the ELF basins. This analysis would have been more questionable with large core ECPs.

The principal outcome is that no polysynaptic attractors appear between sulfur or chlorine and palladium core attractors. This means that the bond is not of the shared-electron type. Owing to the high chemisorption energy calculated for both S and Cl, the Pd−X bond could not be explained as merely due to van der Waals interactions, and we interpret it as a charge-transfer bond. We have seen that, unlike sulfur, the chlorine atom prefers the 2-fold adsorption sites. Following the hypothesis of a donor−acceptor bond, the 2-fold coordination of chlorine is due to the allowance for this atom of a unique p orbital to receive electrons. Therefore, in order to optimize the superposition between this orbital and the palladium d orbitals, the bridging position between two metal atoms is prefered by chlorine. The molecular orbital analysis supports this hypothesis: actually, we have found that chlorine contribution to the

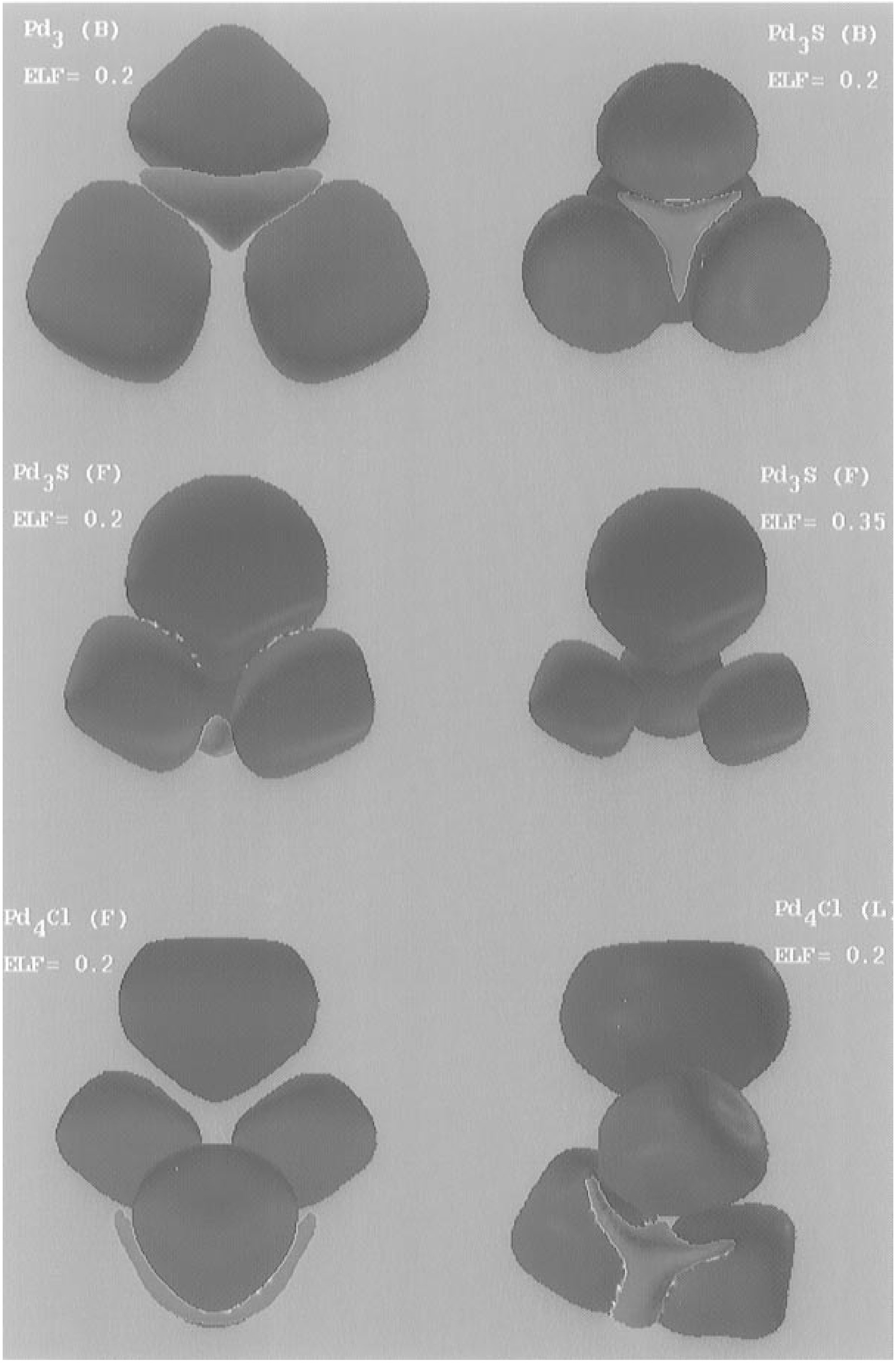

Figure 9. Localization domains for some illustrative clusters. The color code characterizes the nature of the attractor defining the domain: magenta denotes core, red denotes valence monosynaptic (lone pairs), and green denotes valence polysynaptic (shared electrons) attractors. These graphic renderings have been obtained with the visualization software SciAn.[42] F: "front" view. B: "bottom" view. L: "lateral" view.

HOMO is always done via one p orbital, whereas for sulfur it is done via two p orbitals (for $n \geq 3$).

The polysynaptic domains appearing between palladium atoms are significative of a weak shared-electron interaction for the intermetallic bond. The synaptic order is two for two-palladium systems and three for $n \geq 3$.

4. Conclusions

Sulfur interaction with transition metals is an important topic because of the ability of this atom to act as an inhibitor of their catalytic activity. Theoretical research could provide new insight into the nature of the sulfur poisoning effects and the role of additive compounds such as chlorine that increase the thiotolerance.

We have therefore performed hybrid Hartree−Fock/density functional calculations to study the chemisorption of sulfur and chlorine atoms on palladium. The considered clusters are models for small metal particles like the ones found on carriers of oxide insulators (keeping in mind that support effects are not represented), or even for the defects and border edges present on the surface of bigger metal particles and bulk metals. A complete geometry optimization was carried out, allowing the occurrence of low-symmetry structures. This approach allowed us to compare consistently the results obtained with different cluster sizes and to follow the size dependence of structural and energetic adsorption properties. We conclude that these properties vary in a monotonous way with an increasing number of palladium atoms and seem to rapidly converge toward limit values. Atomic sulfur prefers to bind at high coordination sites, and the Pd−S bond distance limit was found to be about 2.3 Å, whereas chlorine is 2-fold coordinated and the Pd−Cl limit is 2.5 Å. For both S and Cl the per-bond energy can be estimated to about 25−30 kcal/mol. Sulfur binds more strongly on palladium than chlorine because of its 3-fold coordination. It moreover affects much more the palladium structure, causing a more significant Pd−Pd weakening with respect to the chlorine case.

The enthalpies for the reactions $H_2S + Pd_4 \rightarrow Pd_4S + H_2$ and $HCl + Pd_4 \rightarrow Pd_4Cl + {}^1/_2H_2$, which we can calculate from the total energy differences, are respectively −16.1 and −7.8 kcal/mol. These values would support our hypothesis of H_2S and HCl dissociation on palladium.

The topological analysis of the electron localization function (ELF) pointed out that the Pd−X bond is not of the shared-electron type. We have argued that both sulfur and chlorine adsorption on palladium involve a charge-transfer bond.

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