

## Density Functional Study of the Interaction of Palladium Clusters with Hydrogen and CH<sub>x</sub> Species

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Structures and energies of Pd<sub>n</sub> clusters, with *n* ranging from 2 to 7, were determined through density functional theory. The calculations were performed adopting the B3LYP functionals to calculate the exchange and correlation energy, the effective core potential basis set of Hay and Wadt for the core electrons of palladium (double- $\zeta$  on the valence electrons), and the Dunning/Huzinaga full double- $\zeta$  basis set for the other atoms. It was found that Pd<sub>n</sub> optimized structures are almost regular polyhedrons, all stable as triplets. The calculated geometries were an isosceles triangle for Pd<sub>3</sub>, a distorted tetrahedron for Pd<sub>4</sub>, a bipyramid with triangular base for Pd<sub>5</sub>, a distorted octahedron for Pd<sub>6</sub>, and a bipyramid with pentagonal base for Pd<sub>7</sub>. The interaction of these clusters with atomic hydrogen in terms of structure and energy was also considered. All structures are stable with the hydrogen lying outside of the cluster, preferably 3-fold coordinated. A maximum of the hydrogen bond energy was found for a cluster containing three palladium atoms. Increasing the number of palladium atoms diminishes the bond energy until a value near the experimentally measured adsorption energy for atomic hydrogen on a palladium surface is reached. Similarly Pd<sub>n</sub>-CH<sub>x</sub> species, with *x* being between 0 and 3, were studied: all hydrogenated fragments are located outside the metal cluster, with coordination depending on the number of hydrogens, whereas the carbon atom is included in the cluster thus modifying its structure. If the influence of the support on reactivity can be neglected, palladium clusters can be viewed as a model of a supported catalyst with extremely dispersed particles, and some considerations about the coke formation process can be made. In particular this analysis shows that coking is favored by increasing cluster size.

### Introduction

Palladium is one of the most used metal catalysts. Although there are a series of processes based on palladium as a homogeneous catalyst, its main use is as a heterogeneous one. Its peculiar power to absorb hydrogen makes palladium a common catalyst for hydrocarbon hydrogenation (e.g., palladium supported on alumina catalyzes the hydrogenation of acetylenes contained in the effluent from steam cracking of hydrocarbons), but other applications are, for example, selective reduction of functional groups, vapor-phase synthesis of vinyl acetate from ethylene, oxygen, and acetic acid (Pd on SiO<sub>2</sub> or Al<sub>2</sub>O<sub>3</sub>, promoted with K), oxidation of methane to methanol (Pd on Al<sub>2</sub>O<sub>3</sub>), and production of vitamin K<sub>4</sub> (palladium membrane); finally palladium enters in the composition of catalysts for the control of vehicle engine emissions (together with platinum and rhodium).<sup>1–3</sup>

Essentially three factors influence the properties and performances of supported metal catalysts: spillover, interaction between the metal and support, and metal particle size. Spillover consists of the transport of an active species (i.e., atomic hydrogen) sorbed or formed on a first phase (i.e., the metal) onto another phase (i.e., the support) that does not sorb or form the species under the same conditions. In this way, the support is no longer inert and neither serves to promote the inherent activity on the metal, but it is participating directly in the transport, exchange, and reaction with the spilt-over hydrogen.

As an example, palladium and platinum are efficient dopants to be added to a metal oxide for the sake of lowering its temperature of reduction by hydrogen.<sup>4</sup>

The nature of the support can affect the physical structure of a deposited metal and its chemical properties in a variety of ways, one of these being the particle size distribution and particle shape (flat or “raftlike” particles). Investigations have been conducted on SMSI (i.e., strong metal–support interactions), choosing as model catalysts platinum supported on titania. The result was the so-called “decoration model”, extended afterward to all noble metals and to other supports: it was observed that titania species migrate from the support onto the platinum where they block surface sites, change crystal morphology, partially encapsulate the metal, and perhaps cause electronic effects or create new surface sites where titania and platinum meet.<sup>5</sup> Palladium on alumina systems prepared from different metal precursors and by various methods were studied by IR spectroscopy and XPS: it resulted that the dispersion of palladium is controlled by the electron transfer from the support to the supported metal; analogous results were found for platinum and nickel.<sup>6</sup>

The metal particle size is directly connected with the amount of active sites present on the catalyst surface. A variation in the aggregate dimension induces a change in the ratio between the atoms present on the surface and those in the bulk and in the coordination state of the surface atoms. Accordingly the electronic configuration of these surface atoms also changes, thus influencing the catalytic properties. For example, it was found that the reaction rate for the hydrogenation of ethylene

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over Pt/SiO<sub>2</sub> or Pt/Al<sub>2</sub>O<sub>3</sub> has a maximum at a particle size of about 0.6 nm.<sup>7</sup>

In this past decade much progress has been made in putting together all these different aspects of supported metal catalysts, especially due to the wide application of physicochemical methods in catalyst characterization.<sup>6</sup> However the characterization of catalyst surfaces is still insufficient to clarify all aspects of heterogeneous catalysis essentially because there is a gap between analytical and operative conditions (especially a pressure gap), so that the species observed could differ from those present in reaction conditions. Moreover, it is difficult to analyze the influence of a specific parameter, as usually different catalyst properties are involved at the same time. Finally, not many techniques can be applied in situ with the consequence of seeing the catalyst only before and after, not during, the reaction, thus losing the possibility to observe surface intermediates.

Because of that, and because of the increase in computer speed, quantum chemistry calculations are more and more adopted in order to investigate the reactivity of catalysts.<sup>8</sup> In this work, palladium clusters have been chosen as a simplification of the heterogeneous catalyst, and the influence of cluster size, above individuated as one of the fundamental factors affecting the properties of catalysts, on hydrogen activation and cluster reactivity toward hydrocarbons have been approached theoretically.

Metal clusters represent an effective model for palladium-based catalysts since palladium is frequently deposited on a support as microaggregates, a form which lies in an intermediate position between single atoms and the bulk solid. Of course, in this way the influence of the support on catalyst performances is neglected, at least at the first steps of the work, but the attention is focused on the relation between catalyst activity and metallic active site dimension. In fact the activity of a supported catalyst does not usually vary regularly with the number of atoms in the clusters, but maxima emerge at specific dimensions. As an example, the disproportionation of cyclohexene to cyclohexane and benzene at 303–323 K on Pd/Al<sub>2</sub>O<sub>3</sub> has been studied and three different maxima appeared corresponding to 4, 10–11, and 20–21 metallic atoms in each ensemble.<sup>9</sup> Out of the catalysis field, clusters of sodium, synthesized at high temperature, show the greatest stability when consisting of 8, 20, 40, and 58 atoms.<sup>10</sup>

## Methods

In this work, quantum chemistry was applied to investigate the geometrical structure of palladium clusters and their interaction, in term of structure and energy, with hydrogen and CH<sub>x</sub> species ( $x = 0-3$ ). In a simplified approach, isolated palladium clusters have been considered, thus neglecting the effect of the support on which palladium is usually deposited. The method adopted was density functional theory (DFT), having the advantage over other more sophisticated ab initio methods of scaling with the square or cube of the problem size, depending on the implementation. In all the calculations the exchange and correlation energies were calculated with the three-parameter Becke Lee–Yang–Parr hybrid (B3LYP) functionals.<sup>11a,b</sup> The chemically inert core orbitals of palladium were represented with the effective core potentials of Hay and Wadt,<sup>12a,b</sup> which include relativistic effects on valence electron, while the outermost orbitals (4d<sup>10</sup>, 4s<sup>2</sup>, 4p<sup>6</sup>, 5s<sup>2</sup>) were described with a double- $\zeta$  basis set;<sup>12c</sup> for hydrogen and carbon the Dunning/Huzinaga full double- $\zeta$  basis set was adopted.<sup>12d</sup> Such basis set will be briefly referred to as Lan12DZ in the following.

**TABLE 1: Method Validation: Comparison between Calculated and Experimental Bond Strengths of Pd–Pd and Pd–H**

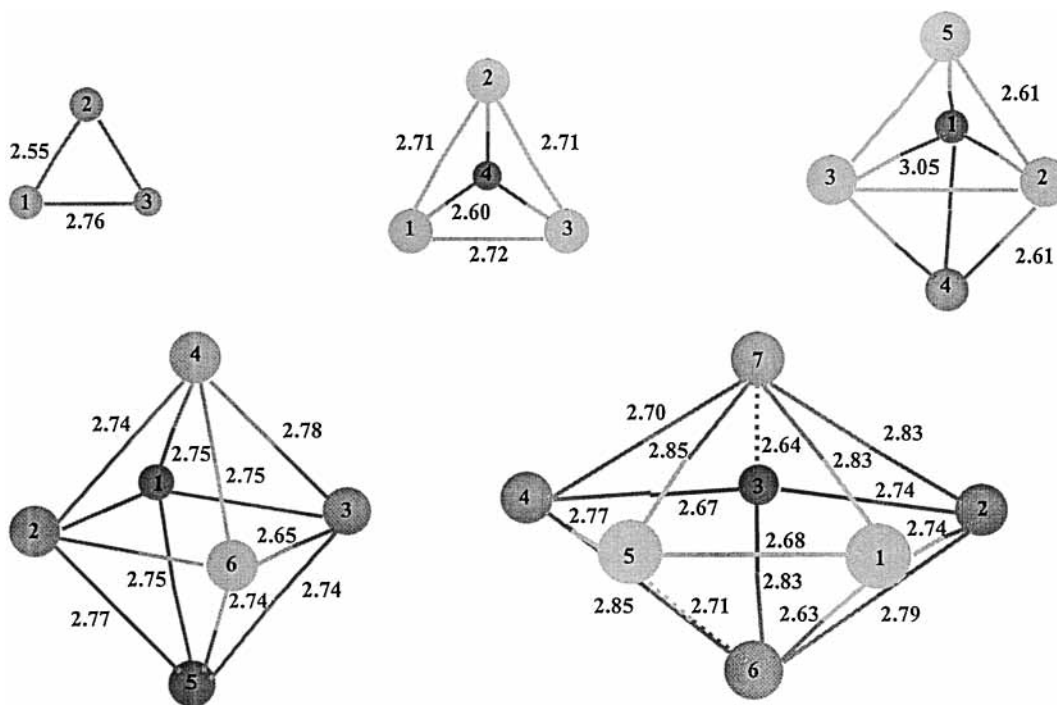
Pd–Pd		Pd–H	
method	bond strength (kcal/mol)	method	bond strength (kcal/mol)
B3LYP/Lan12DZ	22.1	B3LYP/Lan12DZ	57.7
B3LYP/SDD	30.6	B3LYP/SDD	32.6
B3LYP/CEP-121G	54.1	B3LYP/CEP-121G	27.5
B3PW91/Lan12DZ	21.1	B3PW91/Lan12DZ	56.2
experimental	23.9 ± 3.6	experimental	55.9 ± 6

All the calculations were performed with the Gaussian 98 program suite.<sup>13</sup>

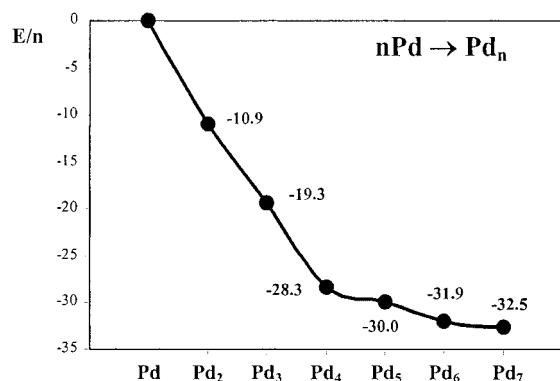
Not many computational theoretical works have been published on transition metals, essentially because of their high number of electrons leading to time-consuming calculations and also for the presence of d-orbitals partially occupied; fortunately this second problem does not affect palladium, which presents a complete 4d-shell. Two different hybrid functionals (B3LYP and B3PW91<sup>14</sup>) and three basis sets (Lan12DZ, CEP-121G,<sup>12c</sup> and SDD<sup>12f</sup>) were considered. Bond strengths for Pd–Pd and Pd–H were calculated and compared with experimental data;<sup>15</sup> the energies were left uncorrected for the zero-point energy. From an inspection of the results reported in Table 1, the basis set giving best predictions in terms of comparison with experimental data is Lan12DZ (e.g., SDD and CEP-121G overestimate Pd–Pd bond energy and underestimate Pd–H bond energy). The two hybrid functionals (i.e., B3LYP and B3PW91) give almost equal results, with B3LYP being slightly better. The choice of B3LYP and the Lan12DZ basis set was supported by other successful calculations on similar palladium clusters performed by Valerio and Toulhoat.<sup>16</sup> In this work they studied the geometrical structures and energies of Pd<sub>n</sub> clusters with a number of atoms between 2 and 6. Their ground states were found to be all triplets and all with a regular structure; in particular Pd<sub>3</sub> and Pd<sub>4</sub> are a triangle and distorted tetrahedron, respectively, both with C<sub>2v</sub> symmetry, while Pd<sub>6</sub> is a distorted octahedron with D<sub>4h</sub> symmetry. Cui et al.<sup>17</sup> chose the hybrid functional B3LYP and a double- $\zeta$  basis set to study the activation of H<sub>2</sub> and CH<sub>4</sub> on Pd and Pt dimers and trimers. They found that B3LYP calculations give reliable results for geometry and binding energy of the dimers compared to complete active space second-order perturbation (CASPT2) theories calculations and that increasing the basis set size had a small effect.

Bedrow and Pacchioni focused their attention on the influence of a support on metal clusters: they made calculations based on the DFT method to study Pd atoms and dimers supported on a (110) surface of TiO<sub>2</sub>, simulated by means of (TiO<sub>2</sub>)<sub>n</sub> clusters, and their interaction with CO. They found that the preferred kind of Pd adsorption on rutile, i.e., on O or 5-fold coordinated Ti sites, depends on the coverage, but in any case it does not influence the interaction of the Pd<sub>2</sub>/TiO<sub>2</sub> system with CO.<sup>18</sup>

Calculation approaches different from DFT have been applied in the study of transition metal clusters. Balasubramanian has carried out multiconfigurational self-consistent field (MCSCF) followed by multireference singles plus doubles configuration interactions (MRSDCI) calculations, including up to 2 million configurations, on low-lying electronic states of Pd<sub>3</sub>; the spin-orbit contributions to the various states of Pd<sub>3</sub> were calculated using a relativistic configuration interaction (RCI) method. Ten nearly degenerate electronic states of Pd<sub>3</sub> were found, with the <sup>1</sup>A<sub>2</sub> state as the most stable (ground state); they all exhibited acute triangular equilibrium structures.<sup>19</sup> Stave and DePristo



**Figure 1.** Structures of Pd<sub>n</sub> clusters ( $n = 3-7$ ) with distances reported in Å and angles in deg.



**Figure 2.** Energies of formation of Pd<sub>n</sub> clusters from  $n$  Pd atoms (kcal/mol) divided by the cluster dimension.

applied the corrected effective medium (CEM) theory to investigate the geometrical structures of Ni<sub>n</sub> and Pd<sub>n</sub> clusters ( $n = 4-23$ ). The authors pointed out that the structures of transition metal clusters do not resemble fragments of the bulk crystal or the structures assumed for rare gas clusters. Particularly, they are characterized by nearly spherical shape, large range of nearest-neighbor distances, very high coordination, and large electron density about their core atoms. Moreover several of the most stable structures are highly symmetric: clusters from 4 to 7 atoms have  $T_d$ ,  $D_{3h}$ ,  $O_h$ , and  $D_{5h}$  symmetry, respectively.<sup>20</sup> Fahmi and van Santen have determined these same structures through a DFT method, using the Amsterdam density functional program (quasi-relativistic spin-unrestricted, frozen-core calculations; triple- $\zeta$  basis set for palladium).<sup>21</sup>

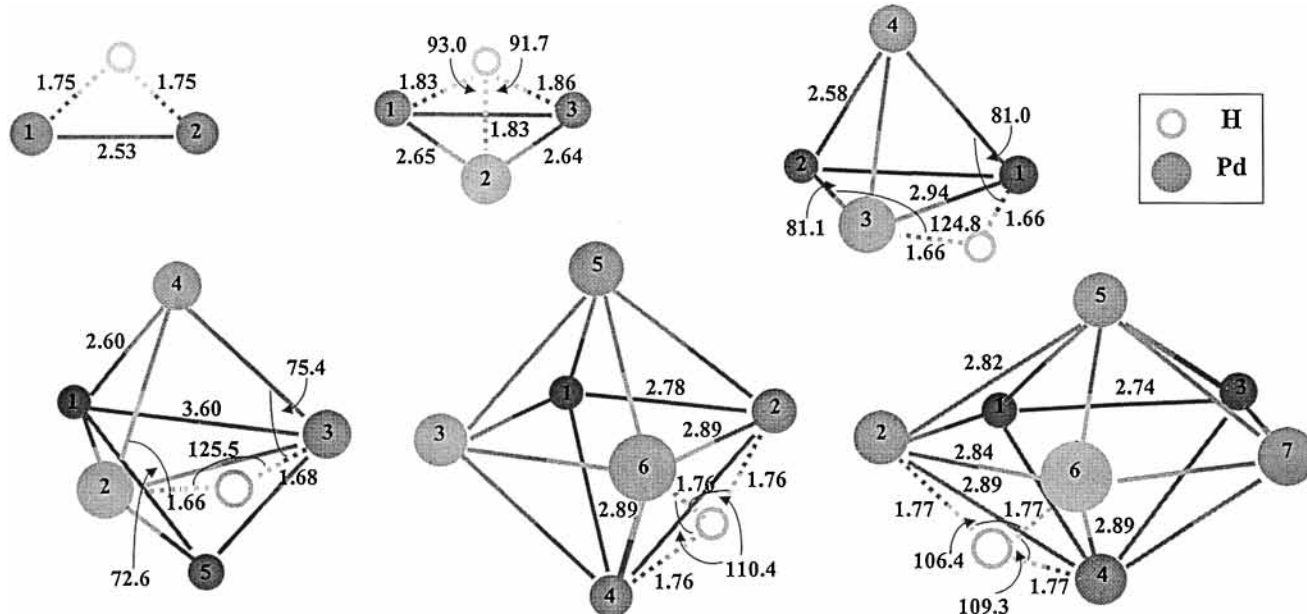
The strategy adopted in order to determine the stable structures of the palladium clusters here considered, with and without adsorbed species, consisted in hypothesizing different starting geometries with nonsymmetric structures. The guess structure was successively optimized adopting the Berny algorithm and redundant internal coordinates. No molecular symmetry was imposed to the cluster geometry in the calcula-

tions, which increased the computational cost and the number of parameters that had to be optimized. On the other hand, the eventual symmetry of the optimized structure resulted as an output of the optimization process. The stability of all the optimized structures was verified computing the force constants and vibrational frequencies. An optimized structure was considered stable only if possessing no imaginary vibrational frequencies. It must however be pointed out that this approach does not exclude the existence of an isomer with a lower total energy. In fact the optimized structures are conditioned by the initial guess geometries, and even if different structures from which starting the optimization were considered, this does not imply that the full configuration space has been explored.

## Results and Discussion

Different structures and energies of isolated palladium clusters and palladium clusters with adsorbed hydrocarbon species were considered.

Pd<sub>n</sub> clusters ( $n = 2-7$ ) were first studied; the obtained structures with relevant bond lengths and angles are reported in Figure 1. Despite the results already obtained by Valerio,<sup>16</sup> who adopted a calculation strategy similar to ours, on the geometry of palladium clusters, we started from structures far from regularity and minimized their energy. Our calculations confirmed those reported in the literature: all stable structures are triplets, in agreement with the calculations reported by Nakatsuji<sup>22</sup> and Fahmi and van Santen,<sup>21</sup> and quite symmetric, deviating from a higher degree of symmetry owing to the Jahn-Teller effect. In detail, Pd<sub>3</sub> is an isosceles triangle with Pd(2)–Pd(3) as base; Pd<sub>4</sub> is a distorted tetrahedron with the Pd(1,2,3)–Pd(4) bonds, all of 2.60 Å, shorter than the other Pd–Pd bonds; Pd<sub>5</sub> is a bipyramid with an equilateral triangle comprising Pd(1)–Pd(2)–Pd(3) as base with vertexes equidistant from Pd(1), Pd(2), and Pd(3); Pd<sub>6</sub> is a distorted octahedron with the Pd(4)–Pd(5) axes longer than the other two; and Pd<sub>7</sub> is a bipyramid with a pentagonal base. Figure 2 reports the energy change relative to the formation of each Pd<sub>n</sub> cluster from the isolated palladium atoms divided for the number of palladium



**Figure 3.** Structures of Pd<sub>n</sub>H clusters ( $n = 2-7$ ). The geometrical parameters defining the Pd cluster structure were omitted since they are similar to those of the Pd<sub>n</sub> clusters.

**TABLE 2: Electronic Energy and Energy Differences (reported in absolute value) between Singlets and Triplets for Pd Clusters Containing up to 6 Atoms**

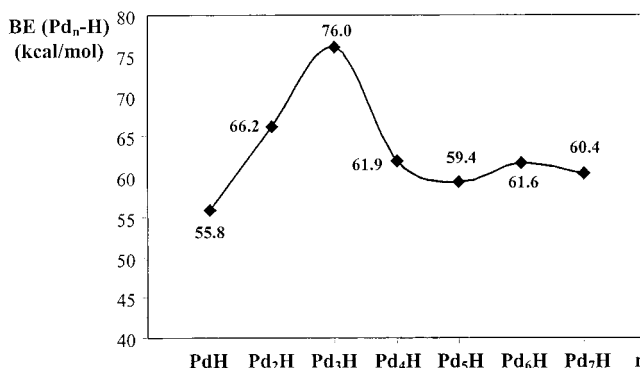
Pd cluster	energy (Hartrees)		$\Delta E$ (kcal/mol)
	singlet	triplet	
Pd <sub>2</sub>	-253.4362	-253.4488	7.9
Pd <sub>3</sub>	-380.2048	-380.2142	5.9
Pd <sub>4</sub>	-506.9843	-507.0106	16.5
Pd <sub>5</sub>	-633.7525	-633.7770	15.4
Pd <sub>6</sub>	-760.5405	-760.5552	9.2

**TABLE 3: Bond Energies (kcal/mol) of Pd Clusters with CH<sub>x</sub> Species**

	CH <sub>3</sub>				CH <sub>2</sub>				CH				C			
	CH <sub>3</sub>	CH <sub>2</sub>	CH	C	CH <sub>3</sub>	CH <sub>2</sub>	CH	C	CH <sub>3</sub>	CH <sub>2</sub>	CH	C	CH <sub>3</sub>	CH <sub>2</sub>	CH	C
Pd	41.69	57.38	69.49	48.59	Pd <sub>5</sub>	33.66	74.51	116.93	131.23							
Pd <sub>2</sub>	44.39	78.40	110.97	114.07	Pd <sub>6</sub>	33.53	75.01	110.43	131.80							
Pd <sub>3</sub>	48.22	92.64	128.22	130.29	Pd <sub>7</sub>	33.16	71.87	119.31	144.10							
Pd <sub>4</sub>	33.53	76.11	110.72	126.09												

atoms present in the cluster. This energy tends to a constant value for  $n \geq 5$  (about  $-32.5$  kcal/mol). This can be interpreted observing that increasing the total number of palladium atoms makes the cluster become less size-dependent and progressively tend to behave, toward the addition of a single palladium atom, like the bulk solid. The electronic energy of singlets and triplets and their differences, left uncorrected for the zero point energy, are reported in Table 2 for palladium clusters containing up to six atoms.

Having determined stable structures for palladium clusters, their interaction with a hydrogen atom has been then considered. These Pd<sub>n</sub>-H species are quite interesting, as one of the principal catalytic applications of palladium is in the field of hydrogenation reactions. From the calculations, the hydrogen atom does not modify substantially cluster geometries, and accordingly only bond lengths and angles defining the position of hydrogen with respect to the cluster are reported in Figure 3. Interestingly, considering the affinity of palladium toward hydrogen, it was found that atomic hydrogen adsorbed on Pd<sub>n</sub> is more stable when lying outside of the cluster rather than inside. Different calculations were performed with hydrogen positioned in proximity of the center of the cluster in order to check whether atomic hydrogen is energetically favored to enter inside a cluster



**Figure 4.** Hydrogen bond energies (kcal/mol) in Pd<sub>n</sub>H clusters ( $n = 2-7$ ).

with up to seven atoms, but no stable structure could be found. All clusters are stable as doublets, and the preferred coordination for hydrogen seems to be with three palladium atoms (see Pd<sub>3</sub>, Pd<sub>6</sub>, and Pd<sub>7</sub> clusters), in agreement with experimental data and theoretical calculations reported by Eberhardt et al.<sup>23</sup>

The diagram reported in Figure 4 reports bond energies between the hydrogen atom and each Pd<sub>n</sub> cluster with increasing  $n$ . These energies (BE) were evaluated according to the following expression:

$$BE = (EE + ThE)_{Pd_nH} - (EE + ThE)_{Pd_n} + RT \quad (1)$$

where  $EE$  is the electronic energy of the system and  $ThE$  is the thermal energy (i.e., the sum of the zero-point energy and the energy required to increase the temperature of the species from 0 to 298 K). The highest stability belongs to Pd<sub>3</sub>H (76.0 kcal/mol), which confirms the preference for the 3-fold coordination. With  $n \geq 4$  an almost constant value of 61.0 kcal/mol characterizes the clusters; this is consistent with the value of 62.8 kcal/mol measured by Conrad et al. with temperature-programmed desorption of hydrogen adsorbed over a Pd(111) surface.<sup>24</sup> Chen et al. have investigated the structures and dynamics of hydrogen-palladium/nickel clusters ( $n = 2-10$ ) using both classical and quantum mechanical Monte Carlo methods (embedded atom method). They found metal clusters

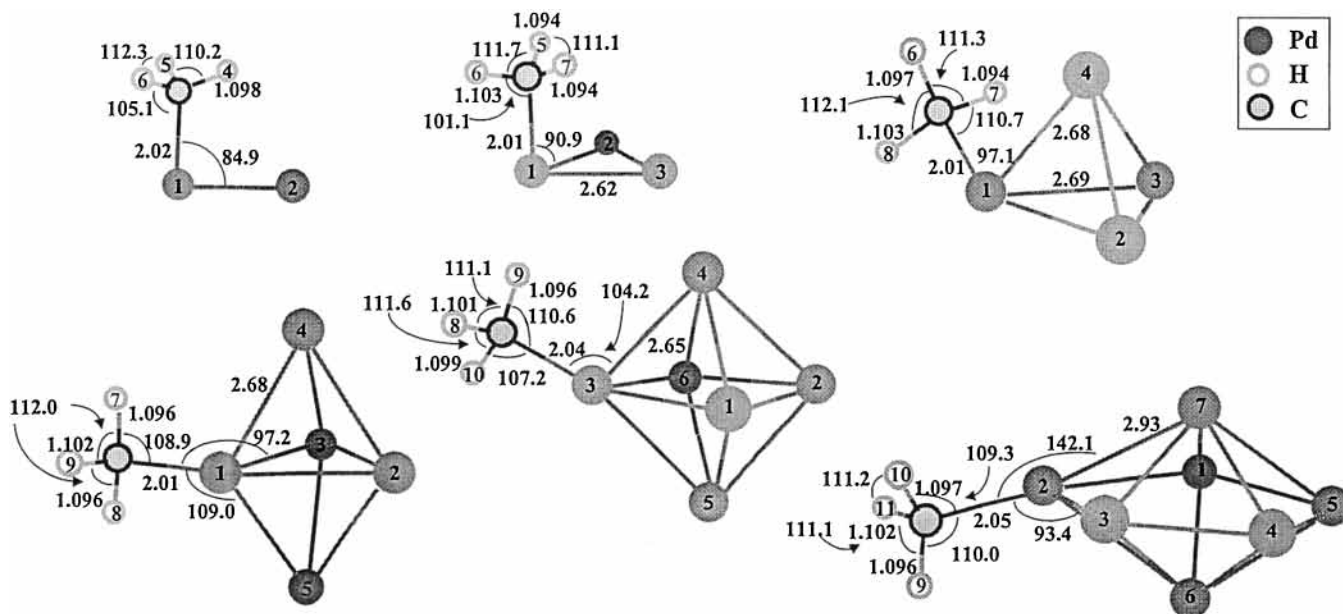


Figure 5. Structures of  $\text{Pd}_n\text{CH}_3$  clusters ( $n = 2-7$ ).

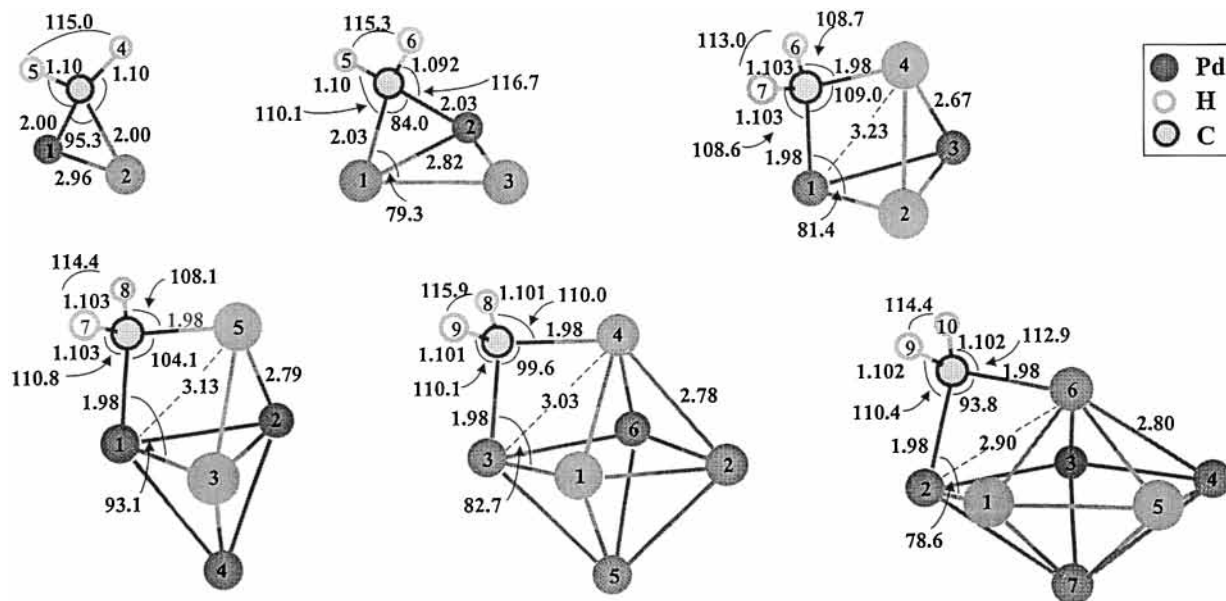


Figure 6. Structures of  $\text{Pd}_n\text{CH}_2$  clusters ( $n = 2-7$ ).

with polyhedral structures that incorporate, differently from our calculations, the hydrogen atom in tetrahedral or octahedral sites. Hydrogen binding energy decreases increasing cluster dimension, but even for  $\text{Pd}_{10}\text{H}$  it is still quite far from the experimental value of 64 kcal/mol (88.8 kcal/mol with classical method and 79.6 kcal/mol with quantum mechanical method).<sup>25</sup> These results differ from ours for we found that the energy of interaction of hydrogen with palladium clusters is already constant and relatively near the experimental value for clusters with more than three palladium atoms (Figure 4). This suggests that the interaction of hydrogen with palladium is mainly local, provided that hydrogen is lying on the surface and not inside the cluster and, therefore, not very much influenced by the cluster dimensions. The agreement with experimental data seems to confirm that hypothesis.

To complete the analysis of palladium clusters as catalysts for hydrogenation reactions also hydrocarbons were considered. Structures and energies of  $\text{CH}_x$  species adsorbed on the clusters were evaluated, choosing methane as the hydrocarbon for sake

of simplicity. It was assumed that  $\text{CH}_4$  dissociatively adsorbs on palladium clusters, so  $\text{Pd}_n\text{CH}_3$ ,  $\text{Pd}_n\text{CH}_2$ ,  $\text{Pd}_n\text{CH}$ , and  $\text{Pd}_n\text{C}$  species, with  $n$  varying between 2 and 7, have been studied.

Figures 5–8 show the obtained stable structures with reported significant bond lengths and angles. As for atomic hydrogen, clusters maintain almost their original structure when  $\text{CH}_x$  species,  $x = 1-3$ , are considered. The coordination of the carbon atom changes with the number of bonded hydrogens:  $\text{CH}_3$  is localized on a single palladium atom (coordination number 1),  $\text{CH}_2$  bridges two palladium atoms (coordination number 2), and  $\text{CH}$  is located in the center of a cluster face as the single hydrogen atom (coordination number 3). This variation is due to a change in the hybridization of carbon in the hydrocarbon radical (i.e.,  $\text{sp}^3$  for  $\text{CH}_3$ ,  $\text{sp}^2$  for  $\text{CH}_2$ , and  $\text{sp}$  for  $\text{CH}$ ), which also causes a progressive reduction of Pd–C bond length (e.g., in  $\text{Pd}_5\text{CH}_x$ , Pd–C bond lengths are 2.01, 1.98, 1.95 Å for  $x = 3, 2, 1$ , respectively). Dealing with the spin states,  $\text{Pd}_n\text{CH}_3$  and  $\text{Pd}_n\text{CH}$  species are all doublets in their ground states while  $\text{Pd}_n\text{CH}_2$  species are stable as singlets, with the exception of  $\text{Pd}_2\text{CH}_2$

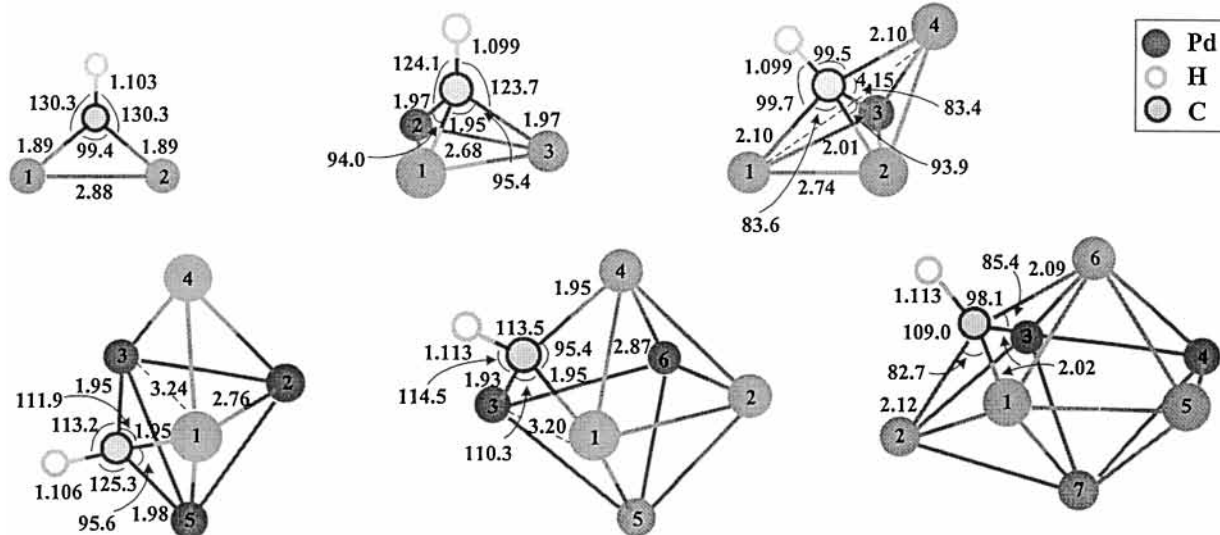


Figure 7. Structures of Pd<sub>n</sub>CH clusters ( $n = 2-7$ ).

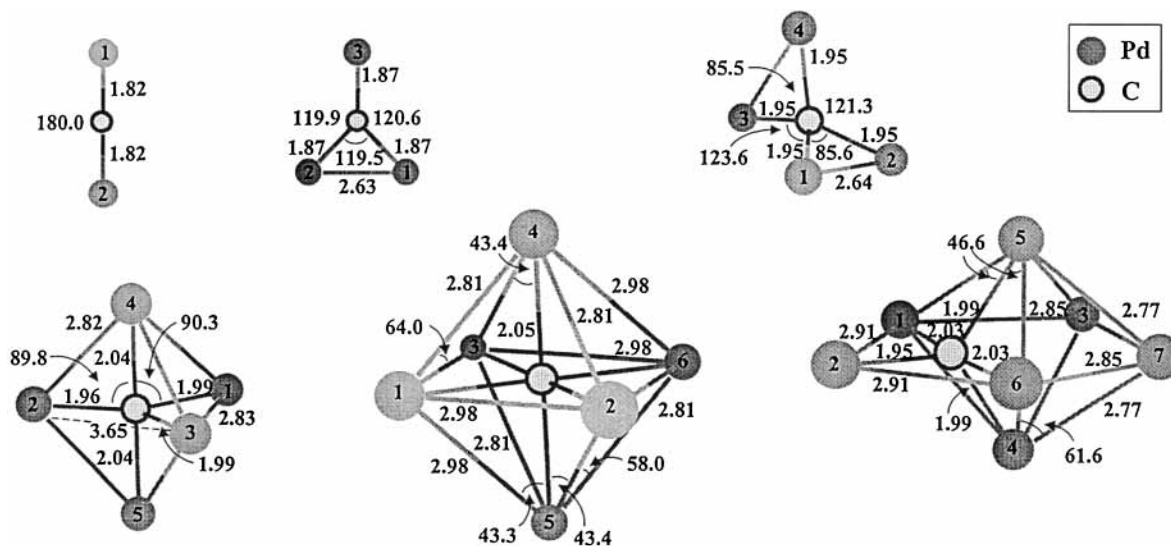


Figure 8. Structures of Pd<sub>n</sub>C clusters ( $n = 2-7$ ).

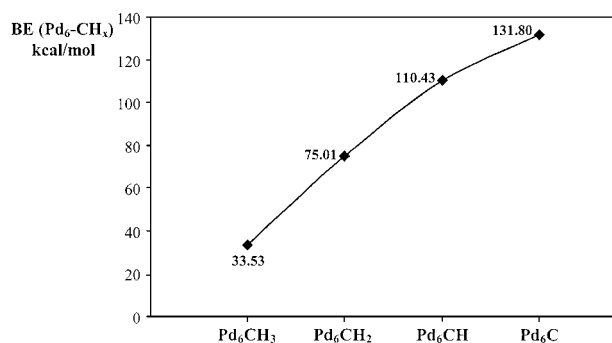


Figure 9. Energies of interaction of hydrocarbon fragments with Pd<sub>6</sub>.

CH<sub>2</sub> which is a triplet. When the coordinated radical reduces to a carbon atom, the situation is slightly different. The carbon atom is now located inside the cluster, thus modifying its structure and becoming part of its network. In the case of Pd<sub>6</sub>C, probably because of the stability of the Pd<sub>6</sub> cluster, two stable structures exist: one with C positioned on an external face of Pd<sub>6</sub> and with spin multiplicity 1 and one with C at the center of the cluster, equidistant from all Pd atoms. This latter structure is a triplet and is more stable than the singlet by about 8.5 kcal/

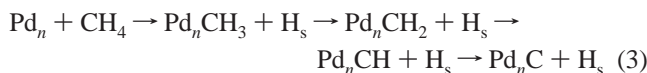
mol. Except for Pd<sub>6</sub>C and Pd<sub>5</sub>C, which are stable as triplets, all Pd<sub>n</sub>C species are stable as singlets.

Bond energies between hydrocarbon radicals and each palladium cluster have been also evaluated, according to the same expression used for Pd<sub>n</sub>H species:

$$BE = (EE + ThE)_{Pd_n+CH_x} - (EE + ThE)_{Pd_nCH_x} + RT \quad (2)$$

Figure 9 illustrates, as an example, the results obtained for Pd<sub>6</sub>-CH<sub>x</sub>; the same trend is followed by all the other clusters. The bond strength progressively increases with the reduction of the number of hydrogens (e.g., 33.5 kcal/mol in Pd<sub>6</sub>CH<sub>3</sub> to 131.8 kcal/mol in Pd<sub>6</sub>C), as should be expected from the increasing carbon coordination number.

The study of the interaction of palladium clusters with methane applies also to another important field of heterogeneous catalysis which is deactivation. One of the principal mechanisms of catalyst deactivation is in fact the deposition of carbonaceous particles, which physically hinders reactants from reaching catalyst active sites. A simplified scheme for this kind of process, usually termed *coking* or *fouling*, is the following:



where  $\text{H}_s$  is a hydrogen atom adsorbed on the catalytic surface and  $\text{Pd}_n\text{C}$  is the deactivated cluster. In this case methane adsorbs dissociatively on the cluster and keeps losing hydrogens up to its total deactivation, instead of reacting, for example, with another adsorbed hydrocarbon species. Via calculating enthalpy changes for each step as a function of cluster dimension, some considerations can be made on the influence of cluster size on coke formation. It must however be pointed out that some care must be placed in the interpretation of the energy changes here reported, since these results were obtained under the hypothesis that the support on which the cluster is adsorbed does not influence its reactivity. This hypothesis has not been verified in the present study, and therefore this aspect must be deepened, either experimentally or theoretically, to determine the extent to which a particular support can influence the reactivity toward hydrocarbons of a dispersed palladium catalyst. Under this point of view this study can be regarded as a first step toward the study of the reaction pathway that leads to the formation of coke in a palladium catalyst.

In Figure 10 the energetic paths for three-, six-, and seven-palladium clusters are reported: the sum of the energies of isolated cluster and methane in the gas phase has been set to zero and the energies of the dehydrogenated systems have been scaled to this value. On  $\text{Pd}_3$  only the dissociative adsorption of methane is exothermic, while all the other steps are more and more endothermic. For  $\text{Pd}_6$  all steps are endothermic except for the last, in which the energy liberated by the inclusion of C in the cluster makes the reaction exothermic. In the case of  $\text{Pd}_7$ , coking formation is endothermic up to  $\text{Pd}_7\text{CH}_2$ , with energies close to the  $\text{Pd}_6$  species. Successively two exothermic steps favor the formation of the completely dehydrogenated species. From these results, deactivation by coking is size-dependent with clusters of higher dimension facilitating the formation of carbonaceous deposits. Accordingly highly dispersed catalysts, with small cluster dimensions, should minimize the formation of coke and therefore have a longer operative life.

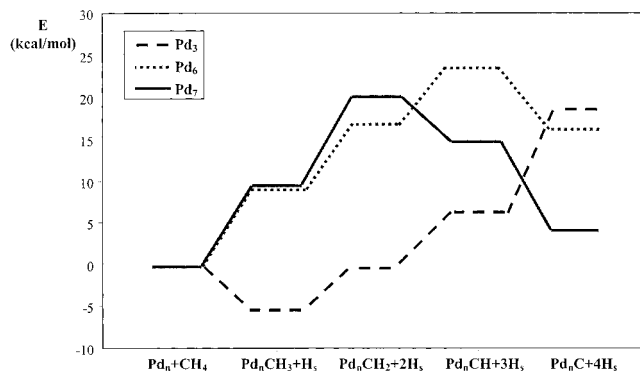
## Conclusions

The structures and energies of palladium clusters containing up to seven atoms were studied adopting DFT. Different functionals and basis sets were considered, and it was found that the best agreement with available experimental data was obtained when the B3LYP exchange correlation functional and the effective core potential basis set of Hay and Wadt for palladium and the Dunning/Huzinaga full double- $\zeta$  basis set for the other atoms were adopted.

In agreement with previous studies, only one stable structure was found for each  $\text{Pd}_n$  cluster. The geometry was similar but not exactly equal to that of the regular polyhedron, and the ground state was always a triplet. Successively the interaction of atomic hydrogen and methane and its fragments with the seven  $\text{Pd}_n$  clusters was investigated.

$\text{Pd}_n\text{-H}$  clusters are stable with hydrogen lying outside of the cluster, 2-fold or 3-fold coordinated. The energy of interaction of hydrogen with palladium increases with the cluster size reaching a maximum value for a cluster with three palladium atoms and then decreases toward a constant value.

Similar results were found for  $\text{CH}_x$  ( $x$  varying between 3 and 0) species adsorbed over  $\text{Pd}_n$  ( $n$  varying between 1 and 7) clusters. For each species stable structures were determined similarly to what had been done for adsorbed hydrogen. All



**Figure 10.** Energies of reaction for the addition of  $\text{CH}_4$  to  $\text{Pd}_n$ . The progressive dehydrogenation leads to the formation of  $\text{Pd}_n\text{C}$  ( $n = 3, 6, 7$ ).

$\text{CH}_x$  species are stable when lying outside the cluster except for carbon, which gives more stable structures when located inside the cluster. On the basis of these results, the energetics of insertion of carbon in palladium was investigated assuming that it proceeds through a progressive loss of hydrogen atoms. This is an important industrial problem since the formation of coke is the process that determines the deactivation of supported palladium catalysts. In this work it was hypothesized that the surface reactivity of palladium clusters dispersed on a support can be assumed to be similar to that of gas-phase palladium clusters. Under such assumption it was found that the insertion of carbon is favored with increasing cluster size; therefore, it was argued that an increase of the catalyst operative life can be probably obtained augmenting the dispersion of palladium over the support or diminishing the mean cluster dimension.

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