

# Theoretical study of the transition from planar to three-dimensional structures of palladium clusters supported on graphene

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Density functional calculations of palladium absorbed on graphene have been performed to study the first stages of Pd coating and/or Pd cluster formation on the graphene surface, a question of great relevance to many experiments. We have found that palladium atoms deposited on graphene have a strong tendency to form clusters. Three-dimensional clusters are more stable than planar clusters and the transition from planar to three-dimensional Pd clusters adsorbed on graphene occurs very early as a function of cluster size, at Pd<sub>4</sub>, as a consequence of the strong Pd-Pd interaction. Palladium might enhance hydrogen storage in porous materials by surface reactions. However, it is a heavy element and the formation of three-dimensional Pd clusters decreases the cluster surface and increases the cluster weight. Hence, a way should be found to prevent clusterization or to disperse finely the palladium atoms deposited on carbon materials. The adsorbed clusters are weakly magnetic, which may be of interest for some applications.

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## I. INTRODUCTION AND MOTIVATION

The study of thin films, nanostructures, atomic chains and clusters of transition metals (TM) supported on surfaces is of great scientific and technological interest, because these nanostructures are small enough to exhibit quantum phenomena and hence, unexpected electronic and magnetic properties can be observed. Some transition metals, which are non-magnetic in the bulk form show ferromagnetism or antiferromagnetism in free and supported clusters, and in thin films. Sc, Ti, V, Pd, Rh, and Ru metals almost satisfy the Stoner criterion of ferromagnetism in the bulk, and hence, they could become magnetic if the density of states at the Fermi level is enhanced either by expanding the lattice parameter or by reducing the atomic coordination number in clusters or nanostructures.

Research on magnetism of TM nanostructures supported on graphene and carbon nanotubes might be very useful to build spin-valve devices. Nanotubes and graphene layers modified by the attachment of metallic particles to their surfaces are potential candidates for chemical nanoscale sensors. These metallic particles are expected to increase the sensitivity toward certain molecules compared to the unmodified nanotubes and graphenes.

Recently, TM atoms and alkali metal atoms deposited on carbon surfaces have focused some attention due to their possible influence on hydrogen storage.<sup>1-8</sup> There is particular interest in hydrogen spillover on carbon materials doped with Pt and Pd,<sup>9-11</sup> because this mechanism enhances the hydrogen storage capacities of the pristine carbon materials. Hydrogen molecules dissociate into atomic hydrogen on these metals and subsequently migrate from the metal particles to the carbon surface. However, simulations<sup>6</sup> have shown that some of these doped materials may suffer from oxidation and aggregation of the metallic atoms, and these processes may diminish the efficiency of metal dopants in enhancing the hydrogen storage capacity. That is, porous car-

bon materials with nucleated TM clusters have lower hydrogen storage capacities than the same materials with the TM atoms finely dispersed on their surfaces. Hence, it is evident that, before studying the electronic, magnetic or hydrogen storage properties of doped carbons, we should investigate first the possible formation of clusters of these metals on the surface of the carbon material.

Ultraviolet photoelectron spectra experiments<sup>12</sup> of Pd, Ni, and Cu atoms deposited on top of graphite and on amorphous carbon showed that these atoms on graphite nucleate into clusters sufficiently large to exhibit bulk properties, even at low coverages, and that, in contrast, they are isolated adatoms on amorphous carbon at low coverages. Ru<sup>13</sup> and Rh<sup>14</sup> atoms on graphite grow laterally until a homogeneous monolayer film is formed. However, for Pd, in spite of its known tendency to form large clusters on graphite, it is not known whether the clusters grow laterally to form large planar islands, similar to Ru and Rh, or rather grow vertically to form three-dimensional clusters, a few layers thick. In an interesting experiment, Sundaram *et al.*<sup>15</sup> modified graphene by electrodeposition of palladium and the metal nucleated at the defects and edges of the graphene layers. The Pd-doped graphene layers were sensitive to hydrogen gas, while the pristine graphene layers were not, and this was attributed to the dissolution and dissociation of H<sub>2</sub> molecules on the Pd nanoparticles. The observed average height of the Pd nanoparticles was 70–90 Å. However, the process of nanoparticle growth is not known. A critically important question is the following: In case that Pd atoms nucleate into three-dimensional clusters on graphene, which is the smallest Pd cluster with a three-dimensional structure?

Sanchez-Paisal *et al.*<sup>16</sup> performed calculations of Zr on graphene, but they only considered planar clusters. Breton *et al.*<sup>17</sup> did calculations for a single Pd atom on graphene, and Uchoa *et al.*<sup>18</sup> studied a homogeneous adsorbed Pd monolayer. Using molecular dynamics and effective interatomic potentials Brault and Moebis<sup>19</sup> have studied the growth of

large Pd clusters (500–3000 atoms) after deposition of Pd atoms on graphite surfaces. They found that cluster growth is sensitive to the roughness of the carbon surface. However, there are not first principles calculations studying the formation of Pd clusters on graphene.

These experimental and theoretical works, and the questions they raise, motivated our investigation on the structure of palladium clusters on top of graphene. We specifically attempt to unveil the critical size for the formation of three-dimensional structures, and find that this critical size is very small. Since we have interest on hydrogen storage on porous materials<sup>20,21</sup> our present results provide basic information for a future study of hydrogen storage in Pd-doped nanoporous materials, especially nanoporous carbons.

## II. METHOD

The graphene layer was simulated as a periodically repeated unit cell consisting of 32 carbon atoms in the  $(x,y)$  plane, forming the well-known honeycomb structure. The Pd atoms are initially placed at different sites on top of the graphene surface and the system is then relaxed. There are three special sites: on top of the center of a carbon hexagon, on top of a C-C bond and on top of a C atom. Density functional theory (DFT) calculations were performed using the supercell method, a plane wave basis set and ultrasoft pseudopotentials, as implemented in the DACAPO code.<sup>22</sup> The pseudopotential for Pd uses a Kr-like core. The local density approximation (LDA) of Vosko, Wilk, and Nusair (VWN)<sup>23</sup> and the generalized gradient approximation (GGA) of Perdew and Wang, PW91,<sup>24</sup> have been used to treat the electronic exchange and correlation effects, and the conclusions for the structure of the adsorbed clusters are the same for both cases. Spin-polarized calculations have been performed in all cases. The optimization of the geometry of the graphene yielded a C-C distance of 1.422, according to the GGA calculations. The cell parameter  $c$  in the  $z$  direction perpendicular to the graphene plane, was 12 Å to minimize interactions between cells. An energy cutoff of 350 eV was taken for the plane wave expansion of the wave functions, and of 1000 eV for the density. The Monkhorst-Pack  $k$ -point set was  $[4,4,1]$  for both clean graphene and graphene with Pd atoms. The value of  $c$ , the cutoffs and the Monkhorst-Pack set were chosen after previous tests, and deliver adsorption energies with a numerical precision of 0.005 eV.

## III. RESULTS

The nucleation of Pd clusters on the graphene surface following the deposition of Pd atoms depends on the relative strength and the interplay between the Pd-C and Pd-Pd interactions. As a test of the theoretical method and to assess the strength of the Pd-Pd bond we first study bulk fcc Pd and the free-dimer Pd<sub>2</sub>. The optimization of the lattice parameter  $a$  of bulk fcc Pd yields the Pd-Pd distances and cohesive energies shown in Table I. Use of a  $[6,6,6]$  Monkhorst-Pack  $k$ -point set was necessary to calculate the cohesive energy with a numerical precision of 0.005 eV. The GGA exchange-correlation functional gives results close to the experimental

TABLE I. Calculated and experimental results for bulk fcc Pd. Magnetic moment  $M$  in  $\mu_B$  units, lattice parameter  $a$  in Å, Pd-Pd distance in Å, and cohesive energy  $E_c$  in eV/atom. Local density approximation (LDA) and generalized gradient approximation (GGA) for exchange and correlation have been used. Experimental data are taken from different sources.

| Functional               | $M$ | $a$  | $d_{\text{Pd-Pd}}$ | $E_c$ |
|--------------------------|-----|------|--------------------|-------|
| LDA                      | 0   | 3.89 | 2.75               | 4.99  |
| GGA                      | 0   | 3.98 | 2.81               | 3.75  |
| Experiments <sup>a</sup> | 0   | 3.89 | 2.75               | 3.94  |

<sup>a</sup>Reference 25.

values. The errors of the GGA calculation are 2.2 per cent for the lattice constant and 4.8 per cent for the cohesive energy. As usual, the LDA gives an overestimated binding energy. By exploring different magnetic solutions we confirmed the known fact that bulk Pd is nonmagnetic.

In the calculations for unsupported Pd<sub>*n*</sub> clusters,  $n=2-5$ , a  $[2,2,2]$  Monkhorst-Pack  $k$ -point set and a fcc unit cell with a parameter  $a=16$  Å were necessary to calculate the binding energy with a numerical precision of 0.005 eV. The results are shown in Table II. Both the LDA and GGA predict that the ground state of Pd<sub>2</sub> is a triplet, in agreement with previous calculations.<sup>26,27</sup> The GGA optimized bond length, 2.52 Å, and the binding energy, 0.65 eV/Pd atom, are consistent with the experimental ones,<sup>28</sup> 2.57 Å and 0.35–0.56 eV/Pd atom. The bond lengths and binding energies of the Pd<sub>*n*</sub> clusters,  $n=3-5$ , also agree with previous GGA calculations.<sup>29,30</sup> For free standing Pd<sub>5</sub> there are two competing structures: the pyramid of square base and the bipyramid of triangular base. The good agreement with the experimental results for bulk Pd and Pd<sub>2</sub> and with the theoretical results for Pd<sub>*n*</sub>,  $n=3-5$ , give us confidence on the method used to study Pd clusters adsorbed on graphene.

Next, we consider the interaction of Pd with graphene. The optimized structures and bonding energies of Pd clusters on graphene, are shown in Table III. For a fixed number of Pd atoms we have simulated different structures, changing the adsorption sites and the shape of the cluster. In Table III we only report results for a few configurations, those lower in energy. The binding energies (per Pd atom) are defined as

$$E_b = [nE(\text{Pd}) + E(\text{graphene}) - E(\text{Pd}_n - \text{graphene})]/n, \quad (1)$$

where  $E(\text{Pd})$  and  $E(\text{graphene})$  are the energies of the free Pd atom and the graphene layer, respectively, and  $E(\text{Pd}_n - \text{graphene})$  is the energy of the system formed by the Pd<sub>*n*</sub> cluster adsorbed on graphene. The most stable location of a single Pd atom, shown in Fig. 1, is in a bridge position on top of a bond between two C atoms. The binding energy is 1.09 eV in the GGA. However, the binding energy of a Pd atom on top of a C atom differs by only 0.05 eV from the former. The DFT calculations of Breton *et al.*<sup>17</sup> (the approximation for exchange and correlation was not specified in the paper) reported a binding energy of 1.1 eV for a single atom on top of an hexagon of graphene, at an equilibrium distance

TABLE II. Calculated and experimental results for Pd<sub>n</sub> clusters,  $n=2-5$ . Total magnetic moment  $M$  in  $\mu_B$  units, Pd-Pd bond length  $d$  in Å and binding energy  $E_b$  in eV/atom. LDA and GGA for exchange and correlation have been used. Results are presented for spin 0 and spin 1 solutions; the ground state is the triplet.

| Cluster                        | Functional              | $M$ | $d$  | $E_b$     |
|--------------------------------|-------------------------|-----|------|-----------|
| Pd <sub>2</sub>                | LDA                     | 0   | 2.50 | 0.69      |
| Pd <sub>2</sub>                | LDA                     | 2   | 2.46 | 0.84      |
| Pd <sub>2</sub>                | GGA                     | 0   | 2.62 | 0.48      |
| Pd <sub>2</sub>                | GGA                     | 2   | 2.52 | 0.65      |
| Pd <sub>2</sub>                | Experiment <sup>a</sup> |     | 2.57 | 0.35–0.56 |
| Pd <sub>3</sub>                | GGA                     | 0   | 2.52 | 1.23      |
| Pd <sub>3</sub>                | GGA                     | 2   | 2.56 | 1.25      |
| Pd <sub>4</sub>                | GGA                     | 0   | 2.64 | 1.60      |
| Pd <sub>4</sub>                | GGA                     | 2   | 2.64 | 1.67      |
| Pd <sub>5</sub> square pyramid | GGA                     | 0   | 2.59 | 1.75      |
| Pd <sub>5</sub> square pyramid | GGA                     | 2   | 2.59 | 1.80      |
| Pd <sub>5</sub> bipyramid      | GGA                     | 0   | 2.67 | 1.76      |
| Pd <sub>5</sub> bipyramid      | GGA                     | 2   | 2.67 | 1.81      |

<sup>a</sup>Reference 28.

$d_{\text{Pd-graphene}}$  of 1.94 Å, to be compared with  $E_b = 0.91$  eV/Pd atom and  $d_{\text{Pd-graphene}} = 2.04$  Å obtained in our PW91 calculations for the same adsorption site. The agreement is reasonable.

The Pd-Pd bond length of a cluster on graphene is larger than the bond length of the corresponding free cluster, as can be seen comparing data from Tables II and III, due to the influence of the graphene substrate. This difference decreases, in general, as the cluster size increases.

For adsorbed Pd<sub>2</sub> the two atoms are located on bridge positions on top of C-C bonds, but those two C-C bonds are second neighbor bonds (see Fig. 1). The binding energy is 1.28 eV/Pd atom, a value higher than the binding energy of an individual Pd atom. This larger binding energy is a result of the Pd-Pd bonding, which is added to the Pd-graphene

bonding, and indicates that aggregation of Pd on the graphene surface is favorable. The distance between the two Pd atoms, 2.75 Å, is larger than the distance in free Pd<sub>2</sub>, 2.52 Å, due to the substrate. We also placed the Pd dimer perpendicular to the graphene surface on three different sites: on top of a carbon atom, a C-C bond and the center of a carbon hexagon, and optimized the structures. These perpendicular configurations of the Pd dimer were metastable, about 0.3 eV/Pd atom less stable than the ground state configuration plotted in Fig. 1. Pd<sub>3</sub> forms a triangle with the Pd atoms in second neighbor bridge positions (see Fig. 1). The aggregation trend continues, since the binding energy increases with respect to Pd<sub>2</sub>, to a value of 1.44 eV/atom.

The case of Pd<sub>4</sub> becomes interesting, because one may consider planar and three-dimensional cluster structures. We

TABLE III. Optimized geometries and bonding energies of Pd clusters supported on graphene. Average distances  $d$  in Å and binding energies in eV/Pd atom, defined in Eq. (1).  $n$  is the number of Pd atoms of the cluster and  $M$  is the total magnetic moment in  $\mu_B$  units. GGA for exchange and correlation has been used.

| $n$ | $d_{\text{Pd-plane}}$ | $d_{\text{Pd-C}}$ | $d_{\text{Pd-Pd}}$ | $E_b$ | Structure     | $M$  |
|-----|-----------------------|-------------------|--------------------|-------|---------------|------|
| 1   | 2.16                  | 2.14              |                    | 1.04  | Pd on C       | 0.00 |
| 1   | 2.16                  | 2.22              |                    | 1.09  | Pd on C-C     | 0.00 |
| 1   | 2.04                  | 2.47              |                    | 0.91  | Pd on hexagon | 0.00 |
| 2   | 2.15                  | 2.26              | 2.75               | 1.28  | Planar        | 0.00 |
| 3   | 2.17                  | 2.29              | 2.77               | 1.44  | Planar        | 0.00 |
| 3   | 2.17                  | 2.29              | 2.77               | 1.44  | Planar        | 0.25 |
| 4   | 2.20                  | 2.32              | 2.77               | 1.55  | Planar        | 0.00 |
| 4   | 2.27                  | 2.39              | 2.72               | 1.56  | Planar        | 1.75 |
| 4   | 2.26, 4.41            | 2.37              | 2.67               | 1.80  | Tetrahedral   | 0.00 |
| 4   | 2.31, 4.44            | 2.43              | 2.67               | 1.84  | Tetrahedral   | 1.89 |
| 5   | 2.26, 4.14            | 2.43              | 2.69               | 1.93  | Pyramidal     | 0.00 |
| 5   | 2.27, 3.04, 4.54      | 2.38              | 2.69               | 1.91  | Bipyramidal   | 1.98 |

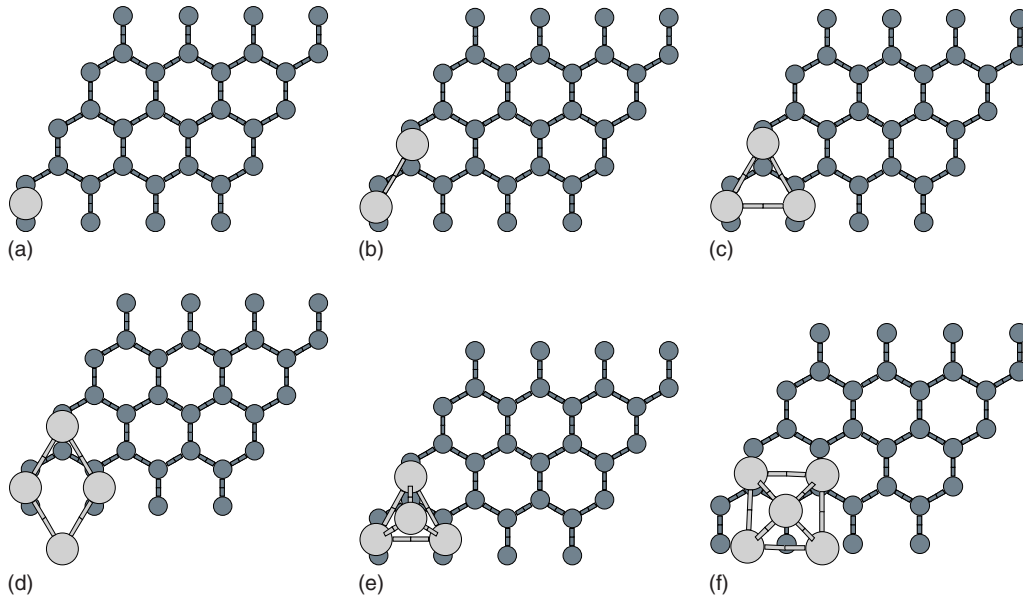


FIG. 1. (Color online) Most stable structure of adsorbed  $\text{Pd}_n$  clusters ( $n=1-5$ ) on graphene. Tetrahedral (ground state) and planar (metastable isomer) structures of  $\text{Pd}_4$ .  $\text{Pd}_5$  is a pyramid of square base.

have obtained, in agreement with previous authors,<sup>29,30</sup> that free standing  $\text{Pd}_4$  is a tetrahedron and planar structures,<sup>29,30</sup> rhombus and square, are higher in energy  $\approx 0.3-0.8$  eV. The question is whether the interaction of the cluster with the graphene layer would favor the planar over the three-dimensional structure. In the planar structure, shown in Fig. 1,  $\text{Pd}_4$  forms a rhombus with two Pd atoms in bridge positions and the other two near C-top positions. However, the most stable adsorbed structure is three-dimensional, a tetrahedral structure with three Pd atoms in bridge positions in direct contact with graphene and the fourth Pd atom bonded to the other three Pd atoms only. The binding energy of the tetrahedral cluster, 1.80 eV/Pd atom (or 7.20 eV/cluster) is substantially larger than the binding energy of the planar isomer, 1.55 eV/Pd atom (6.20 eV/cluster). This occurs because the Pd-Pd bonding is stronger than the Pd-C bonding. The planar configuration of  $\text{Pd}_4$  is a metastable state, but it is clear that the critical size for the formation of three-dimensional Pd clusters on graphene is  $\text{Pd}_4$ .

Not surprisingly, the most stable structure of  $\text{Pd}_5$  is three-dimensional, a pyramid with square base: two Pd atoms of the base occupy positions on top of C-C bonds and the other two Pd atoms are on the carbon hexagons, displaced from the center, as can be seen in Figs. 1 and 2. The fifth atom is on the apex position of the pyramid. A bipyramid is a competitive structure: one edge of its triangular basis lies parallel to the surface and the basis is perpendicular to the graphene plane. The  $\text{Pd}_5$  pyramidal and the bipyramidal clusters supported on graphene have very similar binding energies, being slightly more stable the pyramidal one, as can be seen in Table III. A striking observation is that we have simulated several  $\text{Pd}_5$  planar isomers and all of them evolved spontaneously to form the pyramidal structure. In that process some Pd atoms move 4–6 Å from their initial positions, as can be seen in Fig. 2. This indicates that planar  $\text{Pd}_5$  isomers are unstable against formation of three-dimensional structures, a

fact of great importance that will influence many properties and applications of the deposited clusters. No doubt this strong tendency to form three-dimensional adsorbed structures with just a few atoms has to be taken seriously into account in studies of hydrogen adsorption of Pd-doped carbon nanostructures.

The cluster-graphene distances (distance between the graphene plane and its nearest Pd atoms) increase with the size of the cluster. The same behavior is shown by the nearest Pd-C distances. On the other hand, the Pd-Pd distances vary in a more irregular way and appear to oscillate, a behavior well known for free metallic clusters.<sup>31</sup> The binding energy, defined in Eq. (1), increases with the number of Pd atoms. This reflects the stronger Pd-Pd interaction compared to the Pd-graphene interaction. The Pd-Pd interaction is so strong that when a Pd atom was adsorbed well separated, about 4 Å from an adsorbed  $\text{Pd}_3$  cluster and the system was relaxed, the Pd atom moved spontaneously, driven by the attractive Pd-Pd interaction to form a planar  $\text{Pd}_4$  cluster. That is, formation of Pd clusters on the graphene surface is highly favorable compared to dispersion of the atoms over the surface. The trend to form three dimensional Pd aggregates is explained by the large cohesive energy of bulk fcc Pd, 3.75 eV/Pd atom, compared to the bonding energy of a single Pd

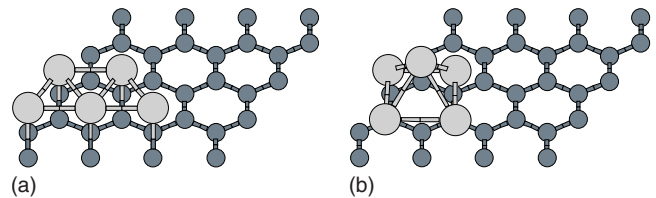


FIG. 2. (Color online) Optimized geometry of a  $\text{Pd}_5$  cluster adsorbed on graphene. The initially planar cluster, left panel, is unstable and spontaneously evolves to form the pyramidal cluster, right panel.



atom on the graphene surface, 1 eV/Pd atom, according to the PW91 calculations. The Pd-Pd distances depend on the shape of the cluster, two-dimensional or three dimensional. The three-dimensional clusters show smaller Pd-Pd distances than the planar clusters with the same number of Pd atoms, because the influence of the substrate is lower.

A single Pd atom and the most stable Pd<sub>2</sub> and Pd<sub>5</sub> clusters on graphene are nonmagnetic, while Pd<sub>3</sub> and Pd<sub>4</sub> are magnetic. In contrast, the ground state of all the free counterparts of these Pd<sub>n</sub> clusters, n=2–5, is a triplet with total magnetic moment  $M=2$  (See Table II).

#### IV. SUMMARY

By performing density functional calculations we have found that palladium atoms deposited on graphene have a strong tendency to form clusters. Planar and three-dimensional Pd<sub>4</sub> can form: a planar rhombus is a metastable configuration, and the ground state structure is a tetrahedron with a triangular face directly adsorbed on the graphene layer. In contrast, the planar structures of Pd<sub>5</sub> are unstable and the simulations indicate that these structures spontaneously evolve to form a three-dimensional cluster, a square

pyramid with the base facing the graphene layer. In conclusion, the transition to three-dimensional structures in Pd clusters adsorbed on graphene occurs very early as a function of cluster size, as a consequence of the strong Pd-Pd interaction. This has implications in the attempts of doping graphitic carbons with Pd with the purpose of enhancing the hydrogen storage capacity of those porous materials. Since Pd is a heavy element, its strong clustering tendency will decrease the gravimetric hydrogen storage capacity unless a way is found to prevent further cluster growth, because only the cluster surface is relevant in the processes leading to an enhancement of the hydrogen storage. Adsorbed single Pd atoms and Pd<sub>2</sub> clusters are nonmagnetic and larger palladium clusters, planar and three-dimensional, are weakly magnetic.

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