Steric and chemical effects on the hydrogen adsorption and dissociation on free and graphene–supported palladium clusters.

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Abstract

Palladium doping enhances the hydrogen storage capacity of nanoporous carbons. The purpose of this work is to asses the effect of the carbonaceous support on the adsorption of hydrogen on Pd clusters. Hydrogen adsorbs on Pd clusters following two channels: molecular adsorption and dissociative chemisorption. These two adsorption channels are investigated on free Pd clusters and Pd clusters supported on pristine and defective (with vacancies) graphene using the Density Functional Formalism. Pd_6 is taken as case study. Free Pd_6 can adsorb twelve hydrogen molecules in the molecular form, a number higher than the nine and eight molecules that can be adsorbed on the cluster supported on pristine graphene and on a graphene vacancy, respectively. However the most stable adsorption channel is, in all cases, the dissociative chemisorption of hydrogen. As the cluster is being loaded with hydrogen, there is a competition between the two adsorption channels. Pd_6 supported on a graphene vacancy is able to dissociate three hydrogen molecules, whereas the free cluster can dissociate up to seven molecules. In both cases, six additional molecules can be adsorbed in the molecular form. The higher saturation limit obtained for the free clusters is explained in terms of the steric and chemical effects of the supporting layer. These effects are of primarily importance to asses the role of the Pd dopant on the adsorption and storage of hydrogen on nanoporous carbons.

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1. Introduction

Hydrogen adsorption on porous carbons is a promising technology for hydrogen storage.[1, 2, 3] However, the technological requirement[4] of storing 5.5 weight per cent of hydrogen at room temperature and moderate pressures is very demanding, and pure carbon materials do not reach that technological target. Some experiments[5, 6, 7] indicate that doping the porous materials with palladium clusters enhances the storage capacity of those materials. Thus, there is a great interest to understand the role played by the Pd dopant on the adsorption and storage mechanism. In previous work we have investigated the adsorption of hydrogen on supported Pd clusters[8, 9, 10] using the Density Functional Formalism. Pristine graphene and graphene with vacancies were considered as suitable models for the walls of porous carbons[11]. The adsorption of hydrogen on free Pd clusters[12, 13] has been also studied. All previous studies focused either on suported[14, 15, 16] or on free clusters; however, to fully understand the role played by the Pd dopant in the adsorption and storage of hydrogen on porous carbons one has to understand also the role of the graphitic support. Thus the aim of this work is to unravel the effect of the graphene support and of the graphene defects on the hydrogen adsorption mechanisms and the hydrogen saturation limit of Pd clusters. With this purpose in mind we have investigated and compared the adsorption and dissociation of hydrogen on free Pd clusters and on Pd clusters supported on pristine and defective (with vacancies) graphene. Pd_6 is taken as a representative cluster. Steric and chemical effects of the supporting layer are investigated. It is important to study all the systems, free and supported clusters, on the same footing for a fair comparison among them. In Section II we present the key technical features of the Density Functional Formalism used in our computer simulations. Section III presents the results and we close with some conclusions in Section IV.

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2. Theoretical Model

Hydrogen adsorption and dissociation on free Pd clusters and on Pd clusters supported on pristine and defective (with vacancies) graphene is investigated using the Density Functional Formalism (DFT). Pristine and defective graphene are considered as appropriate models for the walls of nanoporous carbon materials.

The supercell methodology is used for the DFT calculations, as implemented in the Dacapo code[17]. The graphene layer is represented by a hexagonal supercell in the XY plane with a lattice parameter of 12.33 Å, containing 50 carbon atoms. In the Z direction the supercell is large enough (14 Å) to avoid interactions between the images of the graphene layer in different supercells. The same supercell is used for the free Pd clusters. The calculations are performed using i) Vanderbilt ultrasoft pseudopotentials [18], ii) the generalized gradient approximation of Perdew and Wang (GGA-PW91) [19] for the exchange-correlation functional, iii) a plane waves basis set with cutoffs of 350 eV and 1000 eV for the expansion of the wave functions and the electronic density, respectiely, and iv) four k points distributed in the Brillouin zone following the Monkhorst-Pack scheme [20]. All the calculations allowed for spin polarization.

An extensive search for the lowest energy configurations of free and supported Pd clusters has been performed. For the supported clusters, several orientations (lying on one atom, an edge, or one face) and positions of the cluster with respect to the graphitic substrate have been considered. The preferred configurations of the two lowest energy structures of Pd_6 (OCT and iPB, see below) on graphene are supported on one face of the cluster. In the case of a graphene vacancy, one Pd atom sits at the center of the vacancy and the other two Pd atoms bind to C-C bonds adjacent to the vacancy. Configurations in which two neighbor Pd atoms of the cluster saturated the vacancy were either unstable or too high in energy. In addition, an extensive search for the lowest energy configurations of adsorbed and dissociated hydrogen on free and supported Pd clusters has also been performed. Initial structures included several

Pd$_6$ geometries and hydrogen molecules and hydrogen atoms adsorbed on different vertices, edges and faces of the Pd cluster. All the structures have been fully optimized until the forces acting on all the atoms were smaller than 0.05 eV/Å and the cohesive energies were converged within 10 meV.
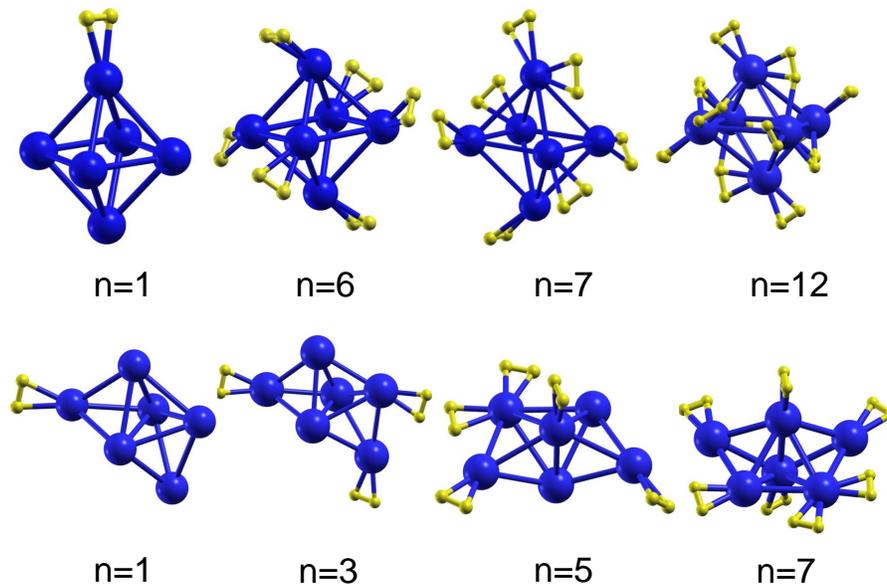
3. Results

Palladium exhibits a strong tendency to aggregate and form three dimensional clusters on the surface of graphene[21] or attached to graphene vacancies.[9] Small Pd$_n$ clusters with $2 \leq n \leq 6$ supported on pristine graphene and anchored to graphene vacancies retain, with minor distortions, the main structural features of the free clusters. The energy ordering of the low lying isomeric structures of the free clusters is also preserved upon deposition of the clusters, but the energy difference between isomers may change. For instance, the lowest energy octahedral (OCT) structure of the free Pd$_6$ cluster is 0.29 eV more stable than the first isomer, which has a structure of an incomplete pentagonal bipyramid (iPB). When supported on pristine graphene the energy difference between the two structures is 0.60 eV, but this difference drops to 0.11 eV when the clusters are anchored on a graphene vacancy. The magnetic moments of the free Pd$_n$ clusters[22] with $n = 2 - 6$ are $\mu = 2\mu_B$. These magnetic moments, however, are quenched down to zero upon deposition of the clusters on graphene vacancies due to the strong cluster-defect interaction, with binding energies of about 5 eV [9]. The interaction of the palladium clusters with pristine graphene is milder, with adsorption energies around 1 eV. Thus, the deposition of the clusters on pristine graphene preserves the magnetic moment for Pd$_3$, Pd$_4$, and Pd$_6$ but leads to zero moments for Pd$_2$ and Pd$_5$.[21] In this paper we investigate the effect of the graphitic substrate and of graphene vacancies on the hydrogen adsorption properties of palladium clusters. We focuss on Pd$_6$ as a case study.

Hydrogen adsorbs on Pd clusters supported on pristine graphene following two different adsorption modes: molecular adsorption and dissociative chemisorption [8] . In the molecular adsorption mode, the hydrogen molecule becomes

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activated and the H-H bond is streched by about 15% from the free molecular bond distance of 0.754 Å but it does not break. In the dissociative adsorption mode, however, the H-H bond is broken and the two H atoms chemisorb independently on the cluster surface. Interestingly, these two adsorption modes are also found on Pd clusters anchored on graphene vacancies [10] and on free Pd clusters [13]. There is a competition between the two adsorption modes as succesive hydrogen molecules are adsorbed on the cluster. Here we investigate how the details of this competition, as well as the hydrogen saturation limit (maximum number of hydrogen molecules that can be adsorbed), depend on whether the Pd cluster is free or supported on pristine or on defective graphene. Steric and chemical effects of the supporting layer are discussed.

Starting with the molecular adsorption of H_2 on Pd_6, the same preferred adsorption sites (on top the Pd atoms) are found for free and supported clusters. In the case of the lowest energy, OCT structure of free Pd_6, succesive H_2 molecules adsorb on top of different Pd atoms. After each one of all the six Pd atoms is decorated with one H_2 molecule, a second H_2 molecule can be accomodated on each vertex of the OCT structure, that is, on each Pd atom, up to a maximum of twelve adsorbed H_2 molecules that completely saturate the free cluster. Notice, however, that for the highest hydrogen coverages (from 7 to 12 molecules) some molecules lean towards a Pd-Pd bond becoming highly activated with H-H distances close to 0.97 Å and the structure of Pd_6 deforms a little from the perfect octahedron. The thirteenth molecule does not bind directly to the cluster and begins to form a second hydrogen layer at a larger distance of about 3.22 Å from the closest Pd atom of the cluster. It has a very small binding energy, 35 meV, one order of magnitud smaller than the binding energies for hydrogen molecules directly bound to the Pd cluster. In contrast with the OCT structure, hydrogen molecules adsorbed on the iPB structure of free Pd_6 begin to share Pd vertices before decorating all the Pd atoms. In fact, the fith H_2 molecule adsorbs on one of the Pd vertices already occupied by another molecule. Finally, additional hydrogen molecules decorate all the Pd atoms. Figure 1 shows some structures of molecular hydrogen adsorbed on
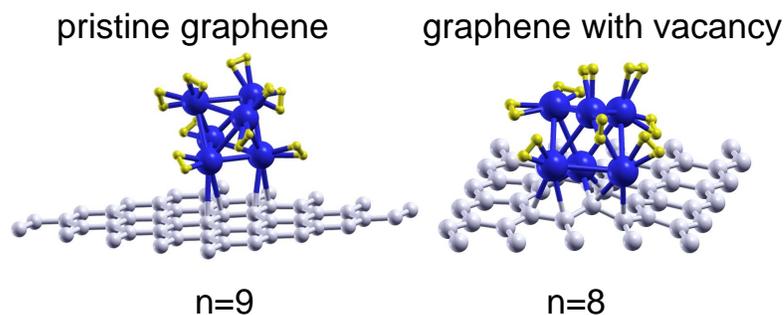
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Figure 1: Optimized structures of molecular hydrogen adsorbed on free Pd_6 clusters. Configurations for Pd_6 in the lowest energy OCT structure (first row) and in the isomeric iPB structure (second row) are shown. n indicates the number of adsorbed molecules. The Cartesian coordinates of all the structures are available in the Supplementary Material.

n=1   n=6   n=7   n=12

n=1   n=3   n=5   n=7

free Pd_6 in the lowest OCT structure and in the first isomeric iPB structure. The iPB structure is slightly more active than the OCT structure: the hydrogen adsorption energies on this structure are $50 - 100$ meV higher than the adsorption energies on the OCT structure. However the OCT structures with adsorbed hydrogen are more stable than the corresponding iPB structures for all hydrogen compositions.

Hydrogen molecules adsorb on the OCT structure of Pd_6 anchored on a graphene vacancy decorating, first, the three Pd atoms which are not in direct contact with the graphene surface (see the structure of the anchored Pd_6 in Figure 2). The forth molecule shares one of the occupied Pd vertices and the fith and sixth H_2 molecules attach, respectively, to the two Pd atoms lying on the graphene surface. Finally, eight molecules saturate the palladium cluster:

Figure 2: Optimized structures of Pd_6 supported on pristine graphene and anchored on a graphene vacancy fully saturated with nine and eight adsorbed hydrogen molecules, respectively. The Cartesian coordinates of all the structures are available in the Supplementary Material.

pristine graphene   graphene with vacancy

n=9   n=8

two attached to each of the three Pd atoms not in contact with graphene and one to each of the two atoms lying on the surface. No molecule adorbs on the Pd atom that saturates the graphene vacancy. Pd_6 supported on pristine graphene can adsorb up to nine H_2 molecules: two attached to each Pd atom not in contact with graphene, and one to each of the three Pd atoms lying on the surface. The succesive molecular adsorption of hydrogen does not change the lowest OCT structure of the free and supported Pd clusters. Figure 2 shows the hydrogen saturated structures of Pd_6 supported on pristine graphene and anchored on a graphene vacancy.
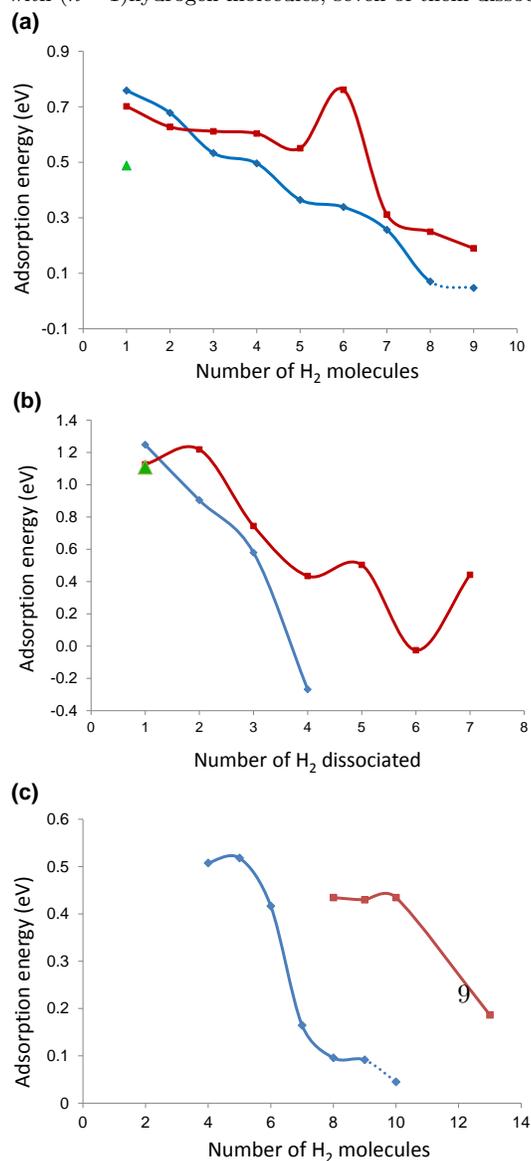
The adsorption energies of hydrogen molecules successively attached on the free Pd_6 cluster and on the cluster anchored on a graphene vacancy are shown in Figure 3.a. In both cases, the adsorption energy of each newly attached

molecule decreases with the number of adsorbed molecules. It is remarkable that the adsorption energies on free and on supported clusters are not too different, except for the sixth molecule. The peak in the adsorption energy for the sixth hydrogen molecule adsorbed on free Pd_6 is due to a change in the magnetic moment of this cluster that quenches down from 2 μ_B to zero. This reduction in the magnetic moment is accompained by the opening of a gap at the Fermi level that stabilizes the cluster. In our opinion, those peculiar magnetic and electronic effects are driven by the very symmetric structure of the $Pd_6(H_2)_6$ cluster as compared to the others.

In summary, the free Pd_6 cluster is saturated with twelve molecularly adsorbed hydrogen molecules. The hydrogen saturation limit is reduced to nine for Pd clusters supported on pristine graphene and it is reduced further down to eight hydrogen molecules for Pd clusters anchored on a graphene vacancy. This reduction in the saturation limit is due, on one hand, to the steric effect of the graphene layer, similar for pristine and defective graphene, that prevents the hydrogen molecules to surround completely the palladium cluster. On the other hand, the strong chemical effect of the defect prevents the hydrogen molecules to adsorb on the Pd atom that saturates the vacancy. The supporting layer, however, seems not to have a major effect on the adsorption energies since the H_2-Pd interaction is quite local (see below the electron density redistribution) and the support does not modify substantially the electronic structure around the Pd atoms, except for the one that saturates the graphene vacancy.

The most stable channel for hydrogen adsorption on free and supported palladium clusters is the dissociative chemisorption of the molecule. In the case of free Pd_6 in its lowest energy OCT structure, the two hydrogen atoms of the dissociated molecule chemisorb on the center of two opposed triangular faces (see Figure 4). The H atoms tend to be as separated as possible on the cluster surface. In the case of Pd_6 supported on pristine graphene, the two H atoms chemisorb, respectively, on two lateral faces that have only one Pd atom in direct contact with the surface. This optimal structure arises from the compromise between separating the H atoms as much as possible and binding
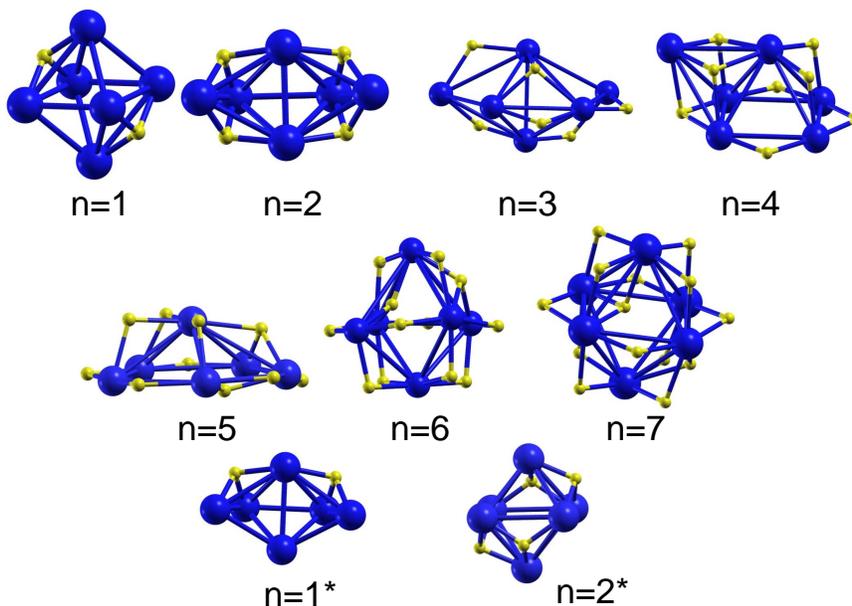
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Figure 3: Adsorption energies of (molecular or dissociated) hydrogen on free Pd_6 (red curves), Pd_6 supported on pristine graphene (green triangles) and Pd_6 anchored on a graphene vacancy (blue curves). (a) Adsorption energy of the nth hydrogen molecule adsorbed on Pd_6 preloaded with $(n-1)$ hydrogen molecules. The blue dotted line indicates that the ninth hydrogen molecule does not bind directly to Pd_6 anchored on a vacancy but begins to form a second hydrogen layer around the Pd cluster at a larger distance. (b) Dissociative chemisorption energy of the nth hydrogen molecule adsorbed on Pd_6 preloaded with $(n-1)$ dissociated hydrogen molecules. (c) Blue curve: Adsorption energy of the nth hydrogen molecule ($n = 4$–10) adsorbed in molecular form on Pd_6 anchored on a graphene vacancy preloaded with $(n-1)$ hydrogen molecules, three of them dissocated and $(n-4)$ molecular. The blue dotted line indicates that the tenth hydrogen molecule does not bind directly to Pd_6 but begins to form a second hydrogen layer around the Pd cluster at a larger distance. Red curve: Adsorption energy of the nth hydrogen molecule ($n = 8$–13) adsorbed on free Pd_6 preloaded with $(n-1)$hydrogen molecules, seven of them dissocated and $(n-8)$ molecular.

(a)

(b)

(c)

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them to Pd faces that have the least number of Pd atoms in direct contact with the graphene layer. When Pd_6 is anchored to a graphene vacancy, one H atom chemisorbs on the triangular face of the Pd cluster not in contact with graphene and the other one on a lateral Pd-Pd bond. This last configuration, however, is not the most stable structure. Instead, the dissociative chemisorption of hydrogen induces a structural change on the anchored Pd cluster from OCT to iPB. The two H atoms chemisorb on two non-adjacent triangular faces of the incomplete bipyramid which are not in direct contact with the supporting layer. The driving force for this structural change is that the iPB structure is more reactive towards hydrogen than the OCT structure. The adsorption energy of hydrogen, in the dissociated state, on the iPB cluster anchored on a vacancy is 0.37 eV higher than on the OCT structure anchored on a vacancy. This energy is sufficient to compensate the lower stability (by 0.15 eV) of the supported iPB structure. On the other hand, the OCT structure of free Pd_6 does not change upon dissociative chemisorption of a single hydrogen molecule. The reason is that, for the free clusters, the difference between the adsorption energy of the molecule, in the dissociated state, on iPB and OCT is reduced to 0.14 eV and does not compensate for the larger energy difference of 0.29 eV between the OCT and the iPB structures.

Dissociative chemisorption of additional hydrogen molecules on Pd_6 anchored on a graphene vacancy does not change the iPB structure of the Pd cluster. This structure is able to dissociate a maximum of three hydrogen molecules. Dissociation of a forth molecule leads to an unstable configuration with respect to desorption of a hydrogen molecule. However, the free Pd_6 cluster is able to dissociate up to seven molecules. The successive chemisorption of hydrogen induces progressive structural transformations of the cluster (see Figure 4). Starting with the OCT structure of the clean (without hydrogen) cluster, successive dissociative chemisorption of one to seven hydrogen molecules leads to OCT, iPB, iPB, decorated square pyramid, pentagonal pyramid, OCT, and OCT structures of Pd_6, respectively. Begining with the sixth chemisorbed molecule, one H atom goes inside the octahedral cage of free Pd_6. It is interesting

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Figure 4: Optimized structures of dissociated hydrogen adsorbed on free Pd_6 clusters. The lowest energy configurations are shown for one to seven dissociated molecules. Moreover, two higher energy configurations (marked with an asterisk) are also shown corresponding to the dissociation of one molecule on iPB and the dissociation of two molecules on the OCT structures of Pd_6, respectively. The Cartesian coordinates of all the structures are available in the Supplementary Material.

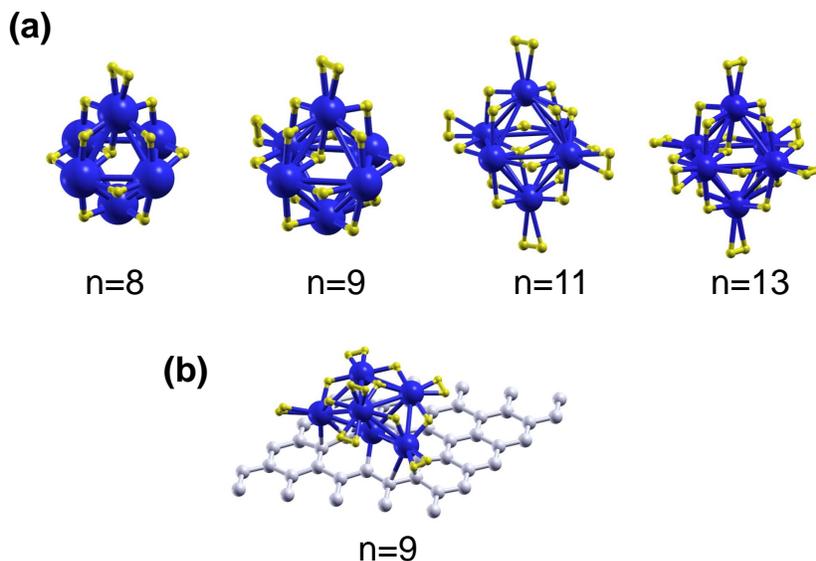n=1   n=2   n=3   n=4

n=5   n=6   n=7

n=1*   n=2*

to notice that this small cluster already exhibits the tendency of bulk palladium to disolve hydrogen. The seventh dissociated hydrogen molecule preserves the H atom inside the octahedral cage.

Figure 3.b shows the chemisorption energies of successive hydrogen molecules dissociated on free and supported Pd_6. The effect of the supporting layer on the dissociation energies of the first three hydrogen molecules is not large. However, the cluster anchored on the vacancy saturates with fewer (three) dissociated hydrogen molecules than the free cluster (seven). Similarly to the case of molecular adsorption, the effect of the supporting layer on the hydrogen saturation limit is two fold: 1) the steric effect, preventing hydrogen from being accomodated

all around the Pd cluster, and 2) the chemical effect, preventing the attachment
of hydrogen to Pd-Pd bonds or Pd faces involving the Pd atom that saturates
the vacancy (see below for an analysis of the interaction between hydrogen and
the Pd cluster).

Although dissociative chemisorption is the prefered channel for hydrogen ad-
sorption on clean (without hydrogen) free and supported Pd clusters, there is a
competition between the two channels as the Pd clusters are being loaded with
hydrogen and, finally, the molecular adsorption becomes more stable. Thus, to
identify the most stable situation, we have investigated both channels (molec-
ular and dissociative) for adsorption of one additional hydrogen molecule (n^{th}
molecule) on a Pd cluster preloaded with $n-1$ molecules. On both free Pd_6
and Pd_6 anchored on a graphene vacancy the dissociative channel is more sta-
ble for adsorption of one and two hydrogen molecules, and the two channels are
almost degenerate for adsorption of the third hydrogen molecule. But from the
forth molecule onwards, the molecular channel is more stable. Actually, it be-
comes the only stable channel on Pd_6 anchored on a graphene vacancy, and six
additional molecules can be adsorbed in the molecular form in this case. Thus,
the cluster becomes saturated with nine hydrogen molecules, three dissociated
and six in molecular form, as shown in Figure 5. The successive adsorption
energies in the molecular adsorption channel on Pd_6 anchored on a graphene
vacancy and preloaded with three dissociated molecules are shown in Figure
3.c. On the other hand free Pd_6 can dissociate up to seven hydrogen molecules.
Starting with the eigth molecule, the molecular adsorption is the only stable
channel and the cluster can adsorb six additional molecules. Thus, the free Pd
cluster becomes saturated with thirteen hydrogen molecules, seven dissociated
and six in molecular form (see Figure 5). Notice that the same number, six, of
additional hydrogen molecules can be adsorbed in molecular form on free and
supported Pd_6 clusters which have been previously fully saturated with disso-
ciated hydrogen. The chemical and steric effects of the supporting layer are not
so apparent in this case, although these effects are clearly present through the
smaller saturation limit for dissociatively chemisorbed hydrogen and the smaller

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Figure 5: (a) Optimized structures for n hydrogen molecules (n=8–13) adsorbed on a free Pd$_6$ cluster. Seven molecules are dissociated and ($n - 7$) are adsorbed in molecular form. (b) Optimized structure of Pd$_6$ anchored on a graphene vacancy fully saturated with nine adsorbed hydrogen molecules, three of them dissociated and six in molecular form. The Cartesian coordinates of all the structures are available in the Supplementary Material.

(a)

n=8   n=9   n=11   n=13

(b)

n=9

total saturation limit of the supported Pd clusters. The succesive adsorption energies of molecular hydrogen on free Pd$_6$ preloaded with seven dissociated molecules are shown in Figure 3.c.

On the other hand, it is interesting to notice that free Pd$_6$ preloaded with one to six dissociated hydrogen molecules can also adsorb additional hydrogen in molecular form. The molecular adsorption energy of one H$_2$ on Pd$_6$ preloaded with n ($n = 1 - 6$) dissociated molecules is about 0.7 eV, almost independent of n. This value, however, is higher than the molecular adsorption energy of 0.4 eV (shown in Figure 3.c) of one H$_2$ molecule on the Pd cluster saturated with seven dissociated molecules.

The nature of the bonding between hydrogen and the Pd clusters can be

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investigated by calculating the electronic density difference $\Delta\rho$ between the system with adsorbed hydrogen and the two separated subsystems, formed by hydrogen on one hand and the free or supported Pd cluster on the other. $\Delta\rho$ for the adsorption of one hydrogen molecule on free Pd_6 is defined as
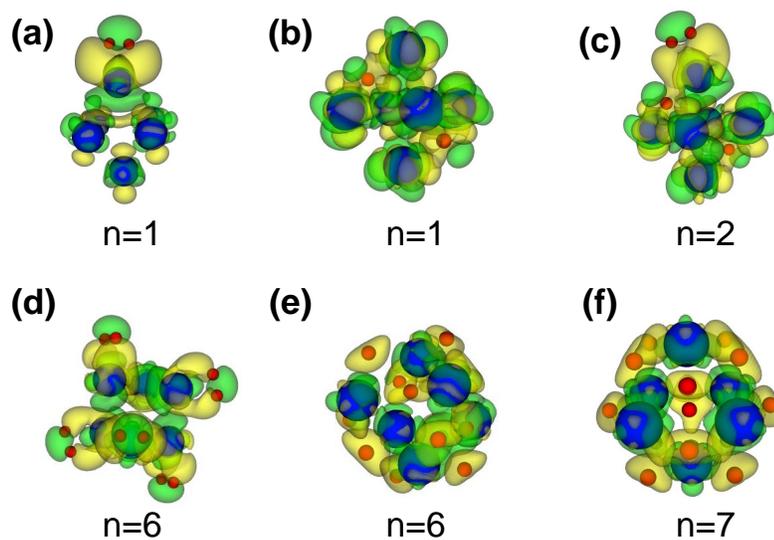
$$\Delta\rho = \rho(H_2 on Pd_6) - \rho(H_2) - \rho(Pd_6) \tag{1}$$

where ρ is the electronic density. In the case of molecular adsorption of hydrogen on a free Pd_6 cluster, an increase (yellow surface in Figure 6) of electronic density between the hydrogen molecule and the nearest Pd atom is observed, indicating a covalent type of bonding[23]; moreover some polarization is also apparent. The bond is localized and involves only one Pd atom. Additional adsorbed hydrogen molecules exhibit each of them a similar type of bonding localized around the attachment site (a Pd atom). However, in the case of dissociative chemisorption of hydrogen, each individual H atom sits in an environment of excess electronic density, characteristic of a metal-hydride type of bonding. The two types of bonding can coexist in the same cluster as it is shown in Figure 6 for the case of two adsorbed molecules, one in the molecular form and the other dissociated. It is interesting to notice that we had found the same types of bonding [10] for the adsorption of hydrogen on Pd clusters anchored on graphene vacancies. This indicates that the supporting layer and the defects do not modify the type of bonding between palladium and hydrogen, because the interaction is local. Notice, however that some regions of the supported Pd clusters, those in direct contact with the vacancy and the graphene support, become inactive for hydrogen adsorption.

4. Conclusions

Doping with palladium has been proposed as a promising way to enhance the hydrogen storage capacity of nanoporous carbon materials. One of the enhancement mechanisms is the direct adsorption and/or dissociation of hydrogen on the Pd clusters doping the material. To better understand the role of the Pd

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Figure 6: Electronic density difference, $\Delta\rho$, between the system formed by hydrogen adsorbed on free Pd_6 and the two separated subsystems, hydrogen on one side and Pd_6 on the other side, for the cases of (a) molecular adsorption of one hydrogen molecule, (b) dissociative chemisorption of one molecule, (c) adsorption of two molecules, one dissociated and the other in molecular form. (d) molecular adsorption of six hydrogen molecules, (e) dissociative chemisorption of six molecules, (f) dissociative chemisorption of seven molecules. The yellow isosurfaces correspond to positive values of the electronic density difference and the green isosurfaces to negative values. Red and blue balls represent H and Pd atoms, respectively.

dopant we have investigated, using the Density Functional formalism, the effect of the graphitic support and of the structural defects existing on the support on the adsorption and dissociation of hydrogen on palladium clusters. To this aim we have compared, as a case study, free Pd_6 clusters with Pd_6 supported on pristine graphene and with Pd_6 anchored on a graphene vacancy.

Two possible adsorption channels of hydrogen on Pd clusters, namely molecular adsorption and dissociative chemisorption, are found on both free and supported palladium clusters. The graphitic support does not modify the type of bonding corresponding to these two channels, weak covalent bond with some polarization for the molecular adsorption, and a hydride type of bonding between the dissociated hydrogen and the metal. The saturation limit for molecular adsorption of hydrogen is higher on free Pd_6 (twelve adsorbed hydrogen molecules) than on Pd_6 supported on pristine graphene (nine) and than on Pd_6 anchored on a graphene vacancy (eight). However, in all cases, the most stable adsorption channel is the dissociative chemisorpion of hydrogen, and a competition between the two channels is stablished as additional hydrogen molecules are adsorbed onto the cluster. Pd_6 anchored to a graphene vacancy can dissociate three hydrogen molecules, whereas free Pd_6 is able to dissociate up to seven molecules. Six more molecules can be adsorbed in the molecular form in both cases. Clearly, more hydrogen can be adsorbed/dissociated in the free Pd clusters than in the supported ones. The supporting surface has two main effects on the adsorption of hydrogen on the Pd clusters: 1) a steric effect that does not allow hydrogen to fully surround the Pd cluster and 2) a chemical effect induced by the defect (vacancy) preventing hydrogen to be adsorbed on the Pd atom saturating the vacancy. In summary, although free and supported Pd clusters exhibit the same two channels for hydrogen adsorption, the effect of the supporting graphitic layer and of the defects have to be considered explicitly to asses the role of the Pd dopant on the storage capacity of nanoporous carbons. Another interesting observation from Figure 3 is that most of the calculated adsorption energies fall in a range that makes possible the desorption step, required for using the stored hydrogen.

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Acknowledgments

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