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Quantum chemical study of neutral and single charged palladium clusters

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Abstract

The extended Hückel (EH) method with an electrostatic two-body correction, has been used in order to determine the structures of small single charged Pd_n clusters with $n = 2$–13 and to compare them with the neutral ones. The results for Pd_2 and Pd_3 are compared with density functional (DFT) calculations. Both cation and anion formations were found to strengthen the clusters due to the bonding character of their HOMO and antibonding nature of LUMO. The twin formation with bond lengths significantly smaller than those in the bulk palladium and in the corresponding neutral particles was found to be the preferential way of growth for anionic clusters; cationic clusters show a more complicated behavior. The promotion of occupation of Pd 5*s* AOs is suggested to be responsible for the formation of 3D structures, whereas the stability of the planar configurations is attributed to the appearance of the vacancy in the valence 4*d*-shell. As a result of stronger intermetallic interaction in charged clusters, both excess and deficit of electron density were found to cause the significant broadness of the *d*-zone. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Theoretical quantum chemical study of the geometrical and electronic structure of ultra-dispersed metal particles is of obvious interest in the theory of crystal growth as well as in inorganic chemistry and catalysis. At present, the most rigorous ab initio studies of particles containing heavy metal atoms are still extremely difficult due to computational expenses, large electron correlation effects, relativistic effects as well as serious SCF convergence problems arising from the existence of a large number of nearly degenerated states. For this reason, semi-empirical methods that allow one to treat rather large transition metal systems, still remain an important tool in theoretical studies of transition metal chemistry. Using the modified extended Hückel (EH) method, we found recently [1] that the twin formation with metal–metal bond lengths slightly smaller than those in the bulk palladium, is the preferential way for Pd_n cluster growth in the absence of the exter-

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nal field, in agreement with experimental [2–10] and other theoretical [11–15] results. In catalytic applications, however, these clusters are usually supported on surfaces of different nature (zeolites, Al_2O_3, activated carbon and so on). For nano-scale Pd clusters with relatively weak intermetallic interaction, one can expect alterations in their geometric structure as a result of the interaction with support. These alterations may be caused by two main reasons: pronounced charging and formation of the new chemical bonds between palladium nano-particles and the support. From the theoretical point of view, it is interesting to examine these two effects independently. In the present work, the EH method with an electrostatic two-body correction, is employed in order to determine the geometric and electronic structure of small single charged Pd_n clusters with $n = 2–13$ and to compare them with the corresponding data for the neutral clusters. The results for Pd_2 and Pd_3 clusters are verified with density functional (DFT) method combined with relativistic effective core potential basis set of double-ζ quality.

2. Computational method

The optimization of the geometry has been performed using a modified semi-empirical EH method. The version of the EH part of the Computer-Aided Composition of Atomic Orbitals (CACAO) [16] program used in our work, was provided by Davide M. Proserpio and Piero Macchi of the University of Milano (Italy) [17] and is described elsewhere [1]. As in our previous study [1], the original EH method [18] with weighted H_{ij} formula [19] is supplemented in the applied scheme by a repulsive term as formulated by Calzaferri et al. [20–22]; this is a modification of the original Anderson's ASED MO approach [23,24]. The ionization potentials and Slater exponents for valence orbitals are used as parameters in EH calculations and play a very significant role in the adequate representation of quantum mechanical forces that determine the physical and chemical properties of the interacting systems. Similar to Ref. [1], in the present work, we apply the original EH approach with the standard Hückel parameters [25]. This approximation reasonably reproduces the experimental geometric and energetic values for Pd_2, PdH, and H_2 molecules and allows us to compare the results with previously studied systems. Since EHT, as a one-electron method, provides no spin elucidation, all calculations were made for the lowest (doublet) state. For up to six atomic clusters, all possible symmetric planar and 3D configurations were considered. For the bigger clusters, only structures with five-fold symmetry and bulk-like arrangements were calculated. The binding energies were computed with respect to the energy of corresponding number of palladium atoms and ions. For the molecular orbital analysis and 3D graphics of the orbitals, the fourth version of the CACAO by Mealli and Proserpio [16] was used.

3. Computational results

Below, we discuss the EH results on the charge influence on the cluster shape, stability, and electronic structure. The minimal energy configuration of Pd_n^+, Pd_n^o and Pd_n^- ($n = 2 \div 13$) clusters, their optimized shortest bond lengths, binding energies per atom and ionization potentials (approximated as HOMO level) are presented in Fig. 1. The structures considered in the present study are the same as those in our previous work [1] and are not reproduced here for the sake of brevity.

The optimal Pd_n^- cluster configurations are equivalent to the neutral clusters with the exception only of Pd_5. For this neutral cluster, the structure of triangular bipyramid was found to be 0.0006 eV less stable than square pyramid, whereas for the Pd_5^-, the former configuration is 0.019 eV more stable than the latter one. The cationic clusters with six or less atoms, on the other hand, tend to form planar structures. As the cluster grows, the energetic difference be-

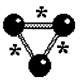
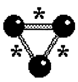
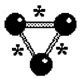
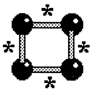
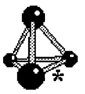
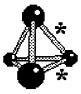
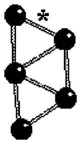
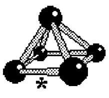
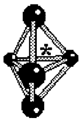
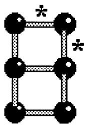
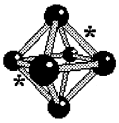
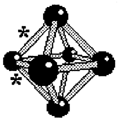
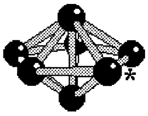
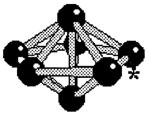
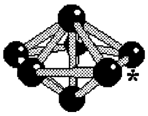
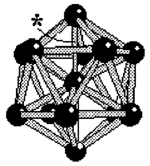
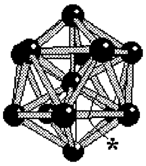
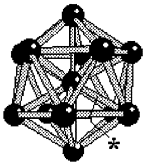
n	parameter	Pd_n^+	Pd_n^o	Pd_n^-
2	r_e BE/at IP	 2.221 0.307 -11.43	 2.489 0.068 -11.62	 2.191 0.685 -8.67
3	r_e BE/at IP	 2.318 0.350 -11.16	 2.529 0.113 -11.45	 2.346 0.720 -9.26
4	r_e BE/at IP	 2.316 0.336 -11.14	 2.570 0.144 -11.50	 2.427 0.711 -9.68
5	r_e BE/at IP	 2.355 0.323 -10.98	 2.519 0.167 -11.40	 2.434 0.666 -9.89
6	r_e BE/at IP	 2.372 0.308 -10.95	 2.595 0.182 -11.46	 2.496 0.635 -10.11
7	r_e BE/at IP	 2.386 0.293 -11.22	 2.562 0.195 -11.44	 2.478 0.596 -10.19
13	r_e BE/at IP	 2.325 0.302 -10.94	 2.564 0.230 -11.24	 2.529 0.482 -10.63

Fig. 1. Structures of minimal energy Pd_n^+, Pd_n^o, and Pd_n^- isomers calculated by EH method, their optimized bond lengths (r_e [Å]), binding energies per atom (BE/at [eV]) and ionization potentials (IP [eV]) approximated as HOMO level. Presented are the values of the shortest bond lengths (for given symmetry) marked by stars.

tween these minimal energy structures and the 3D ones becomes smaller and the single charged Pd_n^+ clusters with $n \geq 7$ prefer the same configurations as the neutral and negatively charged ones. Such reconstruction of Pd_n cations may be explained by a relative decrease in the electron density deficiency with the increase of the cluster size. However, the excess and deficit of electron density influence the relative stability of different configurations even in the bigger clusters. For instance, for anionic 7, 9, and 13 atomic palladium clusters the pentagonal symmetry configurations and twins are 0.225, 0.191, and 0.089 eV more stable than the clusters with bulk *fcc* lattice. For cationic clusters, the differences are 0.007, 0.056, and 0.075 eV, much smaller than those for the corresponding anions and changing in the opposite direction. For the neutral clusters, a monotonic increase in the binding energy with cluster size was observed.

Both positive and negative charges lead to the strengthening of Pd–Pd bonds, but their influence decreases as the cluster grows. Due to the interaction of these two effects, the single charged cationic and anionic Pd_3 clusters show the strongest intermetallic binding.

Thus, the bigger the cluster, the less pronounced is the influence of the excess of its surface energy and the larger is its tendency to form close packing bulk structure. The positive charging is favorable for the formation of the planar configurations similar to that of bulk palladium surfaces, whereas negative charging makes the five-fold symmetry and multiply twinned structures more stable.

The intermetallic distances in both positively and negatively charged clusters are significantly shorter than those in the corresponding neutral clusters, while the binding energy per atom in single charged clusters is much higher. The smaller the cluster size is, the more pronounced are these changes. The influence of the excess and deficit of electron density on the stability of small Pd clusters may be explained by the analysis of their electronic structure. Fig. 2 presents the typical structure of the frontier orbitals for a Pd_5 cluster with bipyramidal configuration. One can see that the lowest unoccupied orbital (LUMO) is bonding towards all Pd–Pd bonds, whereas the highest occupied one (HOMO) is antibonding. The latter is predominantly composed of Pd $4d$ atomic orbitals on all Pd centers, whereas the former is made of Pd $5s$ AOs of all metal atoms. Both occupations of the LUMO and deficiency in the d-electron density are favorable for the strengthening of Pd–Pd interaction. Moreover, one can see that Pd $5s$ AOs occupation is crucial for the formation of 3D structures of clusters consisting of a few atoms. With reference to the electron configuration of Pd atom $4d^{10}5s^05p^0$, the stability of the planar configurations may be attributed to the appearance of the vacancy in the valence $4d$-shell.

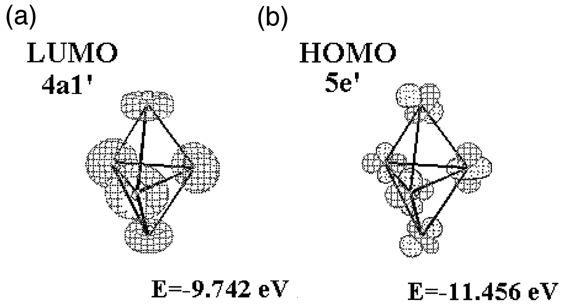


Fig. 2. Lowest empty (LUMO) and highest occupied (HOMO) EH molecular orbitals for Pd_5 cluster with the structure of triangular bipyramid.

Analysis of the electron density distribution shows that both positive and negative charges are uniformly distributed between all metal atoms in small clusters with $n \leq 4$. In planar cation with five atoms, the maximal electron deficit of 0.259 is localized on the symmetric atoms of two-atomic chain and in Pd_6^+, the biggest charge of 0.228 is placed on two central atoms. Atoms in the base of Pd_5^- bipyramid are slightly more charged than atoms at the top. In the pentagonal bipyramid, the excess of electron density of 0.168 appears on the vertex atoms in the anion, whereas in the cation, these atoms have a charge of only $+0.008$. The central atom in the icosahedral configuration keeps the biggest charge of $+0.398$ and -0.174 in the positively and negatively charged clusters, respectively.

Fig. 3 shows the size dependence of the molecular orbital levels for small neutral and single charged palladium clusters in the most stable configurations. One can see that the electronic structure of the single charged Pd clusters differs significantly from that of the neutral ones. A considerable lowering in the LUMO level is clearly demonstrated. In the case of Pd_n^- clusters, this level becomes half-occupied and shows an evident tendency to decrease with increasing n, as in case of the neutral clusters. Positively charged clusters exhibit a similar behavior but not in a monotonic way. As a result of stronger intermetallic interaction in charged clusters, both excess and deficit of the electron density lead to the broadness of the d-zone. Similarly to the non-charged clusters, the top of

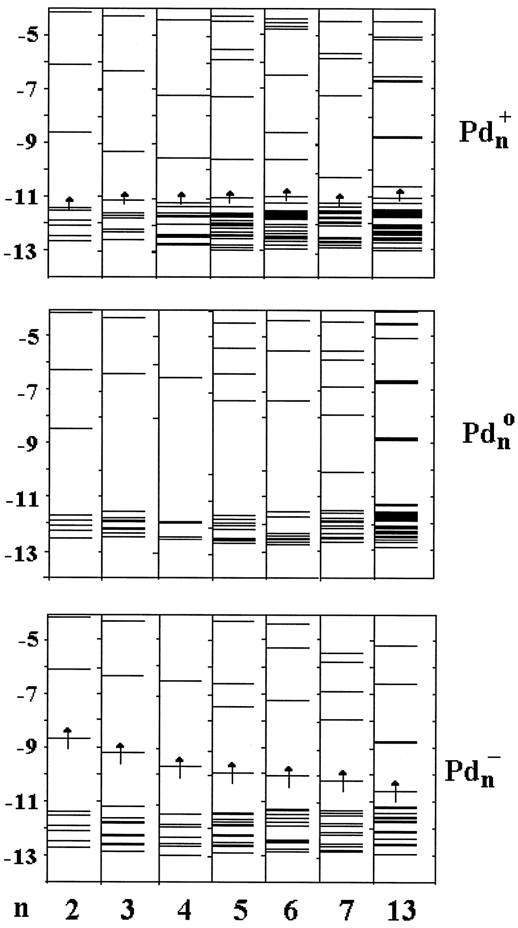


Fig. 3. Size dependence of the EH energy levels for neutral and single charged palladium clusters with minimal energy structures.

d-zone of ions increases, but not monotonically. For both neutral and charged clusters, this level exhibits two local minima at $n = 4$ and $n = 7$. The lowest valence orbital, which presents the bottom of the *d*-zone, significantly drops when moving from Pd_2 to Pd_4 ions, then slowly grows up to $n = 7$ and finally falls for Pd_{13} ions. Due to its breadth, the split in the valence *d*-zone observed for the small neutral clusters is even more pronounced for the ions. The energetic gap between 5*s*- and 4*d*-zones narrows from 2.732 to 0.548 eV and from 2.787 to 0.318 eV for anionic and cationic clusters, respectively, as the cluster grows from 2 to 13 atoms (in comparison with 3.217 to 0.68 eV for the neutral ones).

4. Comparison with DFT calculations

For DFT calculations, we adopted Becke's three-parameter hybrid exchange functional [26] with the correlation functional by Lee et al. [27] (B3LYP) as it is implemented in the Gaussian 94 program [28] and relativistic effective core potential basis set of double-ζ quality by Hay and Wadt (LANL2DZ) [29]. The results obtained in DFT calculations for neutral and single charged two- and three-atomic palladium clusters are shown in Table 1. One can see that the DFT and EH methods show very similar qualitative trends: in both approaches, the binding energy increases with increasing cluster size; single charged clusters are more stable and have shorter inter-atomic distances than neutral ones. In both methods, clusters are weakly bonded: binding energies are 14.20 and 3.14 kcal/mol for Pd_2 in DFT and EH calculations, respectively, in comparison with available experimental values of 17 ± 3 and 26 ± 5 kcal/mol [30] (note that the singlet state is not the most stable for Pd_2). However, the absolute energy characteristics of calculated systems obtained in two approaches differ significantly. The main qualitative disagreement is that EH method shows all negatively charged ions being more stable than positively charged ones while, due to the electron correlation effect, DFT method demonstrates the opposite trend for Pd_2 clusters.

It is generally accepted that the DFT, HF, and EH methods usually predict similar shape, symmetry properties, and energy order of the occupied orbitals (see, for example [31]). In the particular case of small palladium clusters such

Table 1
Optimized bond lengths and corresponding binding energies for neutral and single charged Pd_2 and Pd_3 clusters obtained in DFT calculations

Cluster	Parameter	Pd_n^+	Pd_n^o	Pd_n^-
Pd_2	r_e (Å)	2.661	2.761	2.675
	BE/at (eV)	−1.059	−0.308	−0.944
Pd_3	r_e (Å)	2.756	2.816	2.604
	BE/at (eV)	−1.185	−0.507	−1.503

Table 2
Orbital orders for neutral and single charged Pd$_2$ and Pd$_3$ clusters obtained DFT and EH calculations

	Orbitals	DFT orbitals	EH orbitals
Pd$_2$	Occupied	(SGG) (PIU) (PIU) (DLTG) (DLTG) (DLTU) (DLTU) (PIG) (PIG) (SGU)	(Sg) (Pu) (Pu) (Dg) (Dg) (Du) (Du) (Pg) (Pg) (Su)
	Virtual	(SGG) (SGU) (PIU) (PIU) (SGG) (PIG) (PIG) (SGU)	(Sg) (Su) (Pu) (Pu) (Sg) (Pg) (Pg) (Su)
Pd$_3$ (D$_{3h}$)	Occupied	(A1′) (A2″) (E′) (E′) (A1′) (E″) (E″) (E′) (E′) (A1″) (E″) (E″) (E′) (E′) (A2′)	(E′) (A1′) (E′) (E′) (A2″) (A1′) (E″) (E″) (E′) (E′) (A1″) (E″) (E″) (E′) (A2′)
	Virtual	(A1′) (E′) (E′) (A2″) (A1′) (E′) (E′) (E″) (E″) (E′) (E′) (A2′)	(A1) (E′) (E′) (A2″) (E′) (E′) (A1′) (E″) (E″) (A2′) (E′) (E′)

comparison is not so simple. Due to the large number of nearly degenerate states, significant variations in electronic structure accompany changes in orbital occupations (charge or multiplet state). Table 2 shows the order of the valence orbitals obtained in EH and DFT calculations for closed-shell Pd$_2$ and Pd$_3$ (D$_{3h}$ symmetry) clusters. For Pd$_2$, they are exactly the same, for Pd$_3$, they show only minor differences. Note, however, that these are not the lowest energy states obtained in DFT calculations. Nevertheless, the presented comparison between EH and DFT calculations for Pd$_2$ and Pd$_3$ suggests that qualitative EH results are reliable for other Pd$_n$ clusters. A detailed DFT study of small palladium clusters will be the topic of our future communications.

5. Conclusions

The main result of the present study is that both cation and anion formations strengthen small palladium clusters. The structures of anions are similar to those of the neutral clusters, whereas cations show a more complicated behavior. Negatively charged clusters reveal much more pronounced tendency to form small clusters with pentagonal symmetry due to a larger energetic difference between five-fold and bulk-like arrangements and stronger intermetallic interactions. The deficit of electron density favors the formation of planar configurations. As it was repeatedly shown, different configurations of small palladium clusters have very close energies that allow one to expect their easy interconversions. The results presented indicate that interaction with support might determine the general direction for small Pd clusters growth and make the obtained structures more stable as compared to the corresponding gas-phase clusters. Under the appropriate conditions (temperature, concentration, etc.), the electron-donor supports may be expected to promote the formation of 3D small palladium particles with the pentagonal symmetry. On the contrary, the electron-seeking supports are expected to assist the formation of planar bulk-like configurations. In both cases, the chemistry of small supported Pd clusters is believed to be different from that of the bulk particles due to the shorter intermetallic bond lengths and significant changes in the electronic structure.

Acknowledgements

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