

Size effect of binding energy of the hydrogen atom on $Pt_n(100)$ clusters

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In this paper we have employed the semiempirical PM5 method to investigate a size effect of the binding energy of the H atom on a variety of platinum clusters. The examined clusters of the (100) face symmetry have included up to 101 platinum atoms placed from one to six layers. Our theoretical model of the H atom chemisorption on the $Pt_n(100)$ clusters can be treated as a platinum (100) surface with almost zero coverage of hydrogen. A comparison of PM5 results with the Analytical Cluster Model has been also done.

1. INTRODUCTION

A traditional model of the chemisorption of atoms and simple molecules on metal surfaces is usually based on a cluster approach. This approach assumes that the metal cluster consists of a finite set of atoms, usually of 5 to 100. The cluster model is particularly popular with the simulations of various crystal faces (clusters are cut from an ideal lattice and interatomic distances are kept constant as their bulk values). The presence of an adsorbate on the metal cluster allows us to investigate an interaction between the adsorbate and the cluster surface. Theoretical model often consists of only single atom or one simple molecule adsorbed on the surface. Such systems are very useful for quantum chemistry investigations because the calculations performed within cluster approach are not very time-consuming, therefore more advanced methods can be employed. Moreover, a relatively low cost of such calculations seems to be the greatest advantage of this approach with respect to alternative periodic slab computational technique. The difference of the calculation time between cluster and periodic slab models becomes particularly significant for investigations of

almost zero coverage of the adsorbate. However, many properties of the systems (for example binding energy (BE) and ionisation potential (IP)) examined by means of the cluster model depend on the cluster size, i.e. the number of atoms in the cluster. This is the so-called Size Effect (SE). Fluctuations of the system properties can be sometimes associated with a change of the geometrical structure or shape of the cluster for fixed number of atoms. Such SE is called the Topological Size Effect (TSE).

The SE of the BE and adsorption energy of simple adsorbates on transition metals or semiconductors clusters has recently become a point of interest for a few studies. An adsorption energy (or chemisorption energy; from now these terms are equivalent) often includes in addition a dissociation energy of adsorbate (e.g. for the diatomic molecule $H_2 \rightarrow 2H$) with respect to the BE. Ishikawa et al. [1] studied the chemisorption of CO on the Pt(111) surface by means of the relativistic DFT. This surface has been represented by a variety of Pt_n ($n = 7 \div 22$) multilayer clusters. The authors end up to a conclusion that the calculated CO chemisorption energy converges fast close to the experimental value (measured in a bulk) with an increasing of platinum cluster size. The SE of the energetics of the following reactions: ZrCl₄ with SiO₂ – OH clusters and H₂O with SiO₂ – O – ZrCl₂ was studied by Han et al. [2] by means of the B3LYP hybrid functional. An excellent comparison of the energetics of H₂ desorption and dissociative adsorption processes on Si(001) clusters with the DFT slab calculations has been presented by Penev et al. [3]. In this paper it was shown that very small silicon clusters generally overestimate the adsorption energy of H₂. An impact of SE on the chemisorption process in some hydrogen-silicon systems has been also examined by Burda et al. [4] using the semiempirical CNDO/2 method. In the paper of Koper and van Santen [5] a change of the BE of H atom on Ag_n(111) clusters, where $n = 10 \div 25$, was evaluated by the nonlocal BP86 functional. The SE of the BE of H atom has been also published by Romanowski et al. [6]. The authors have employed semiempirical PM3 method to determine the BE of H on Al_n ($n = 2 \div 32$) clusters. An analysis of the SE in terms of the so-called Analytical Cluster Model (ACM) has been also done in the paper [6].

In all above mentioned papers the size of metal or semiconductor cluster has an influence on the values of binding and adsorption energies. It is worth mentioning that it is possible to remove the SE from the energy values in spite of using of the finite-size clusters in calculations. One has proposed two methods of avoiding of the SE in BE: the Siegbahn group technique [7-9] and the Russier method [10].

In the present paper we concentrate at examining of the SE of BE of the H adsorbed on Pt_n(100) clusters. Such SE has not been investigated till now. We hope that the description of this SE would be valuable for establishing of the

behaviour of quantum chemical methods. Moreover, it can be particularly helpful for interpretation of many theoretical results of platinum clusters applied as contact catalysts.

2. METHODOLOGY OF CALCULATIONS

Quantum chemical calculations have been performed using the semiempirical Modified Neglect of Diatomic Overlap – Parametric Method Number 5 (PM5) [11]. This method is implemented in MOPAC (Molecular Orbital PACKage) as a part of the CAChe (Computer-Aided Chemistry) package [12] and was selected as a proper parametrization of the hydrogen-platinum systems calculations [13].

The examined platinum clusters have a (100) *fcc* symmetry. Pt lattice constant is taken as equal to 3.9242 Å [14]. One can divide these clusters into two groups. The first one contains one-layer clusters built in a planar *XY* coordinate system (see Fig. 1a). The smallest $\text{Pt}_2(100)$ cluster represents a dimer with the bond length equal to a distance between the nearest neighbours of the (100) face. The $\text{Pt}_5(100)$ cluster was taken as a (100) wall of Pt *fcc* lattice. The enlarged $\text{Pt}_n(100)$ clusters, where $n = 13, 25, 41, 61$ and 85 , are built successively by adding of the next atoms in *XY* plane. The second group of the platinum clusters consists of the basic one-layer $\text{Pt}_{16}(100)$ cluster plus multilayer $\text{Pt}_{16+9+\dots}(100)$. It is convenient to describe these clusters in additional *X'Y'* coordinate system (Figure 1a). *XY* system can be easily transformed to *X'Y'* one after a rotation by 45 degrees. The enlarged clusters were composed of 1 to 6 layers (from 16 to 75 platinum atoms, respectively). For instance, $\text{Pt}_{16+9+16}(100)$ denotes the cluster of 41 platinum atoms distributed in three layers: the first one, i.e. the surface one, consists of 16 atoms, the second one – 9 atoms and the third one – again 16 atoms. Hence, in the multilayer clusters there are 16-atom and 9-atom layers, alternatively. We also added the $\text{Pt}_{16+49+36}(100)$ cluster, which was studied earlier [15], to the second group. This 101 atom cluster allowed us to determine an impact of enlarged subsurface layers on the BE of the H.

The H atom is chemisorbed only in a few characteristic positions. These positions have been depicted in Figures 1b and 1c for the *XY*(100) and *X'Y'*(100) symmetry. A proposed distribution of the chemisorption sites results from the assumed cluster approach, i.e. the boundary conditions are inherent in this model because of the neglect of surroundings. It seems that a separation of the chemisorption positions on the edges from the inner sites makes the cluster model more realistic and reliable.

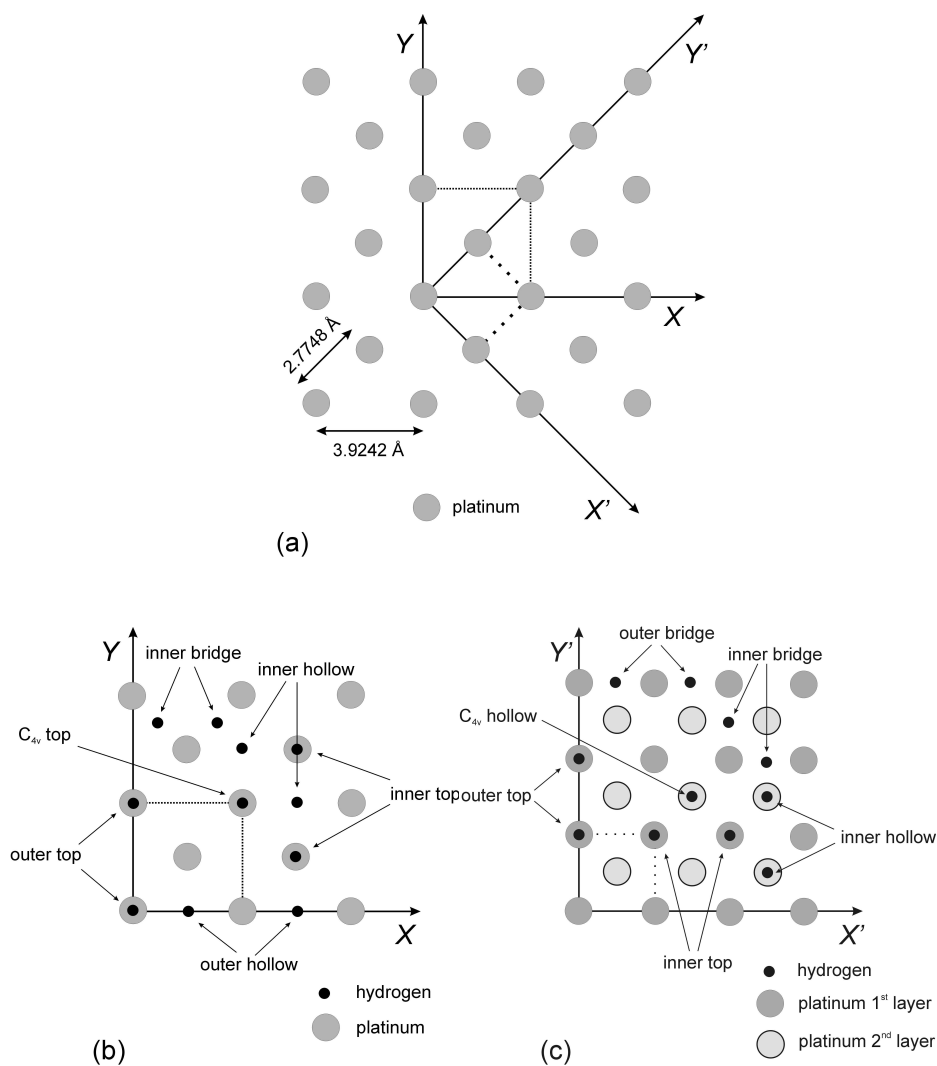


Fig. 1. (a) Scheme of a structure of two kinds of the platinum clusters: $XY(100)$ and $X'Y'(100)$. For the $X'Y'(100)$ system only the first layer (surface) of the platinum atoms has been drawn. (b) Schematic view of the characteristic adsorption sites of the H atom on the $Pt_{13}(100)$ cluster. Two exemplary positions of kinds of adsorption (except for the C_{4v} top, which is marked only one in the cluster (b)) are marked in the figure as black circles. (c) Schematic view of the H adsorption sites on the two-layer $Pt_{16+9}(100)$ cluster. Also two exemplary sites of each kind (except for the C_{4v} hollow) are marked.

For each chemisorption site the BE of H atom on the $Pt_n(100)$ cluster is calculated by means of the following formula:

$$BE = {}^2E_{HPt_n(100)} - ({}^2E_H + {}^1E_{Pt_n(100)}), \quad (1)$$

where ${}^2E_{HPt_n(100)}$, 2E_H and ${}^1E_{Pt_n(100)}$ stand for the total energy of the $HPt_n(100)$ system, the H atom and $Pt_n(100)$ cluster energy, respectively. Upper left indices mean the multiplicities. For each chemisorption site the total energy of the $HPt_n(100)$ system was calculated after an optimization of the H atom height over the platinum cluster surface. More details concerning the calculation scheme of the H atom BE are included in [13].

3. RESULTS AND DISCUSSION

At the beginning of this chapter we focus on investigations of the SE of BE for high-symmetry chemisorption sites. For the $XY(100)$ clusters the highest symmetry position is a top site in the center of the cluster (denoted as a C_{4v} top in Figure 1b). In a case of the $X'Y'(100)$ multilayer clusters the highest symmetry surface chemisorption site is a hollow one in the center of the first layer (denoted as a C_{4v} hollow in Figure 1c). For these two characteristic sites the values of the BE of the H atom are presented in Figure 2. We have also plotted in this figure the ACM curve for comparison.

In the ACM [16] the binding energy (BE) is expressed by the following interpolation formula:

$$BE(n) = a + \frac{b}{\sqrt[3]{n+1}}, \quad (2)$$

where n denotes the number of the metal atoms (Pt in our case) in the three-dimensional system and a and b are the constants. These constants one can obtain from the expressions:

$$a = \lim_{n \rightarrow \infty} BE(n) = BE(\infty), \quad (3)$$

$$b = \sqrt[3]{n'+1} [BE(n') - BE(\infty)]. \quad (4)$$

The $BE(\infty)$ is usually known from an experiment as the BE of H in the bulk of platinum. The n' means the number of the Pt atoms in the smallest cluster for

which the BE was determined. The value BE(*n'*) of the H atom can be calculated by means of *ab initio* quantum chemical method for very small number *n'* = 1,2,3 of the platinum atoms. In the case of hydrogen-platinum systems the experimental value of BE(∞) can be taken as -2.64 eV [17] and BE(*n'* = 1) as -3.2 eV (the dissociation energy of the PtH molecule proposed in [18]). The ACM formalism is completely independent of the chemisorption site symmetry, so only one exemplary ACM curve for both C_{4v} positions is shown in Figure 2.

Considering the BEs of the H atom for the C_{4v} top one can notice a huge difference of the BE of the PtH molecule and the smallest hydrogen-platinum cluster, i.e. HPt₅(100). It suggests that the diatomic molecule of platinum hydride is completely different chemical individual in respect of the HPt₅(100) or HPt₁₃(100) clusters. Passing from Pt₅(100) to Pt₂₅(100) the BE increases quickly (Figure 2) reaching a maximum for twenty five platinum atoms. From Pt₄₁(100) the BE remains practically stable and is equal to -3.47 eV. For this cluster the H atom adsorbed in C_{4v} top position interacts with metal atoms placed in nine different distances. Thus in a case of planar one-layer clusters an attracting contribution of platinum atoms to the H binding energy is not limited only to the nearest neighbours (first and second). It indicates that also further metal neighbours with the C_{4v} top chemisorption position have a significant influence on BE of the H. An existence of the maximum of Pt₂₅(100) cannot be reasonable explained and it is in a strong contradiction with the ACM.

An addition of the second and third layer to the X'Y'(100) sixteen-atom cluster leads to an almost linear decrease of BE in Figure 2. A minimum obtained for three-layer cluster seems to be quite flat and it can follow from an effect of convergence errors. Passing from the four-layer to the six-layer X'Y'(100) clusters we can observe that the BE yields almost the same value of about -3.31 eV. It is interesting that an increase of Pt atom numbers in the second and third layers of the Pt₁₆₊₄₉₊₃₆(100) cluster practically does not change BE of the H atom with respect to Pt₁₆₊₉₊₁₆(100).

A difference of the BE between the C_{4v} top and hollow positions of big, i.e. 50 and more platinum atoms, XY(100) and X'Y'(100) clusters is about 0.15 eV. It remains in good agreement with general observation of a flat and uncorrugated topography of the binding energy surface (BES) [19]. However, the values of the C_{4v} top and hollow BE are rather far from the experimental result (-2.64 eV).

Plots of the H atom BE as a function of the cluster size for the outer and inner top, outer and inner bridge, outer and inner hollow chemisorption sites are shown in Figures 3, 4 and 5, respectively.

One can notice in Figure 3 that for the XY(100) clusters the difference of the outer top BE between the HPt₅(100) and smaller systems, i.e the PtH and HPt₂(100) cluster, is significant.

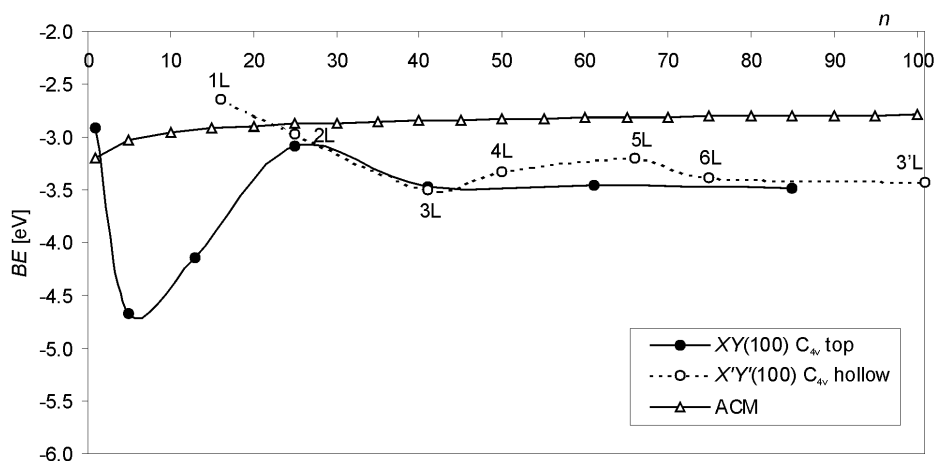


Fig. 2. Binding energy (BE) of the H atom on the $Pt_n(100)$ clusters as a function of the number of n platinum atoms for C_{4v} top and C_{4v} hollow adsorption sites. The number of layers of a given cluster is marked by means of 1L, 2L ... symbols. 3'L stands for the three-layer $HPT_{16+49+36}(100)$ cluster taken from [15].

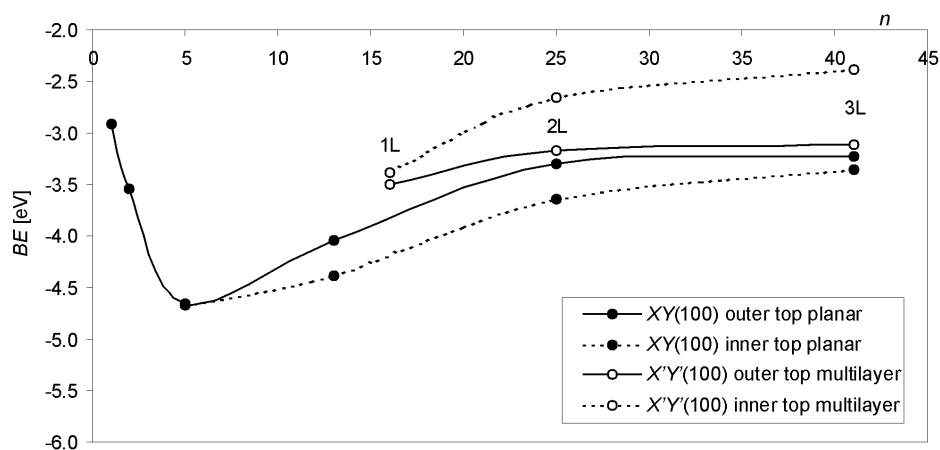


Fig. 3. Binding energy (BE) of the H atom on the $Pt_n(100)$ clusters as a function of the number of n platinum atoms for outer and inner top adsorption sites. The number of layers is marked the same as in Figure 2.

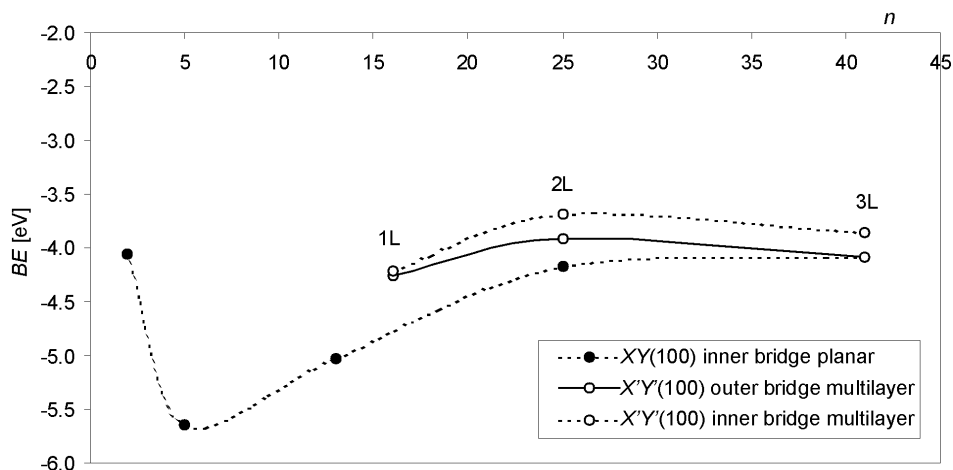


Fig. 4. Binding energy (BE) of the H atom on the Pt_n(100) clusters as a function of the number of n platinum atoms for outer and inner bridge sites. The number of layers is marked the same as in Figure 2.

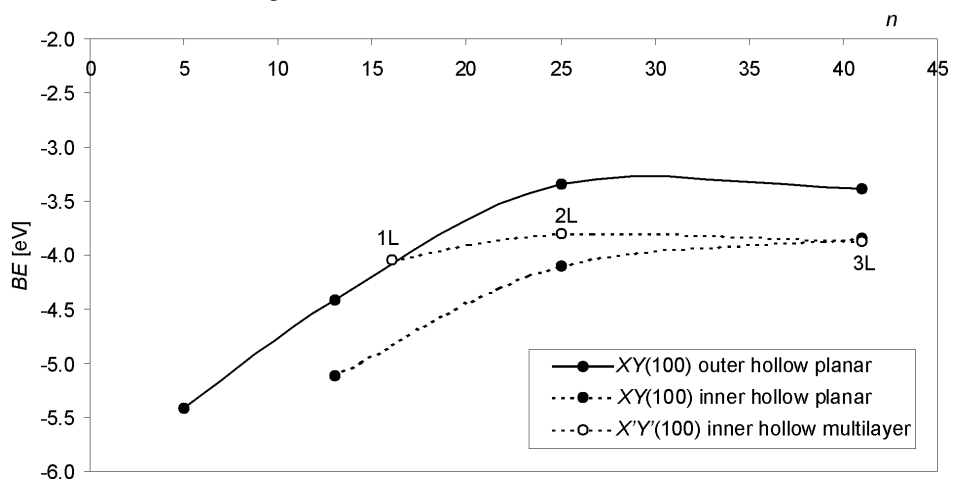


Fig. 5. Binding energy (BE) of the H atom on the Pt_n(100) clusters as a function of the number of n platinum atoms for outer and inner hollow sites. The number of layers is marked the same as in Figure 2.

According to the ACM the BE for Pt₂(100) should be lower than for five-atom cluster. It disagrees with the PM5 result (solid line with black circles in Fig. 3). Outer top BE curve of the XY(100) reaches a minimum for the cluster size equal to five atoms. For bigger clusters the BE of this position converges to the value

of -3.23 eV. In a case of the inner top of planar clusters the BE is smaller than for the outer top one, except for $\text{HPt}_5(100)$, for which BEs of both positions are practically the same. It means that for larger planar clusters the H atom is bound stronger by platinum atoms located inside the cluster than by atoms on the edges. For the biggest examined $XY(100)$ cluster the difference of BE between the outer and inner top is equal to 0.12 eV.

Considering the $X'Y'(100)$ clusters one can find completely different preference of the outer and inner top sites as compared to that of $XY(100)$. Outer top curve of the multilayer clusters is placed beneath the curve of the inner top ones for all sizes of the $X'Y'(100)$. For the basic one-layer $\text{Pt}_{16}(100)$ cluster the BE of the outer top approaches the value of the inner top one. However, an increase of cluster thickness is associated with an increasing difference of the BE between the outer and inner top positions (from 0.1 eV to 0.7 eV for $\text{Pt}_{16}(100)$ and $\text{Pt}_{16+9+16}(100)$, respectively). In a case of the three-layer cluster the value of the inner top BE is equal to -2.38 eV.

In Figure 4 the inner bridge BE curve for the $XY(100)$ cluster seems to be similar with those of the outer and inner top sites, i.e. it has a minimum for the five-atom cluster. When a cluster enlarges, the BE converges fast to the value of -4.09 eV.

Outer bridge position of the $X'Y'(100)$ clusters is energetically more favourable than the inner bridge one. For one-layer cluster the difference of the BE seems to be insignificant but for multilayer it increases to the constant value of 0.23 eV.

The BE of outer and inner hollow is shown in Figure 5. For the $XY(100)$ clusters the BE of the outer hollow is higher than that of the inner hollow. There is a weak lowering trend in a difference of the BE between the outer and inner hollow sites of an enlargement of cluster size (from 0.7 eV to 0.45 eV).

It is surprising that for the $X'Y'(100)$ systems the BE of the inner hollow changes with the increasing number of layers much less than one would expect (practically the same BE value of the one- and three-layer clusters in spite of an increase by 25 in Pt atoms number). For the multilayer, the BE of this site is equal to about -3.9 eV.

4. CONCLUSIONS

In this paper the SE of the BE of H atom chemisorbed on $\text{Pt}_n(100)$ clusters (with $n = 1 \div 101$) is studied. The investigations of the SE should be a standard technique of testing of theoretical methods, particularly semiempirical ones. We can summarize the main results as follows:

- The size of the platinum clusters strongly affects a value of the BE. Considering the platinum clusters with a number of atoms larger or equal to

five we can notice that the PM5 results remain in a qualitative agreement with the ACM. Because of BEs, the diatomic PtH molecule and the HPt₂(100) cluster seem to form quite different class of chemical objects and should not be analysed within the framework of the same model as a bigger system with adsorbed hydrogen.

- The BE for large planar or multilayer clusters are far away from the experimental results of the platinum bulk. It is mainly caused by a theoretical simplicity of the semiempirical methods greatly reducing the computational effort. However, the calculations of large hydrogen-platinum systems by means of *ab initio* methods still remain out of range for most of low-budget workstations.
- Being aware of qualitative similarity of PM5 results with *ab initio* calculations [13], the five-atom platinum cluster gives values of BE not comparable with the results for larger clusters or experiment for a bulk. This cluster always has a minimum of the BE curve. One can say that this cluster seems to be a boundary representing of the cluster model of a hydrogen chemisorption process (kind of a boundary condition). A very low value of the BE for this system might be an effect of undercoordination of the platinum atoms.
- For qualitatively reliable calculations of the BE, by means of PM5, we recommend the calculations of the planar clusters consisting of at least 25 Pt atoms and three-layer clusters containing at least about 40 Pt atoms.

REFERENCES

- [1] Y. Ishikawa, M-S. Liao, C. R. Cabrera, In: *Computational Materials Science*, J. Leszczynski (ed), Theoretical and Computational Chemistry Series, vol. 15, Elsevier 2004.
- [2] J. H. Han, G. Gao, Y. Widjaja, E. Garfunkel, C. B. Musgrave, *Surf. Sci.*, 550 (2004) 199.
- [3] E. Penev, P. Kratzer, M. Scheffler, *J. Chem. Phys.*, 110 (1999) 3986.
- [4] J. Burda, M. Bures, C. Cerny, *Collect. Czech. Chem. Commun.*, 57 (1992) 241.
- [5] M. T. M. Koper, R. A. Van Santen, *J. Electroanal. Chem.*, 472 (1999) 126.
- [6] S. Romanowski, A. Wronka, D. Baldomir, *Bull. Soc. Sci. Lettres Łódź*, 46, Sér. Rech. Déform., 22 (1996) 51.
- [7] P. E. M. Siegbahn, U. Wahlgren, in: *Metal-Surface Reaction Energetics*, E. Shustorovich (ed), VCH, New York 1991, p.1.
- [8] I. Panas, J. Schüle, P. E. M. Siegbahn, U. Wahlgren, *Chem. Phys. Lett.*, 149 (1988) 265.
- [9] P. E. M. Siegbahn, U. Wahlgren, *Int J. Quant. Chem.*, 42 (1992) 1149.
- [10] V. Russier, C. Mijoule, *J. Phys.: Condens. Matter*, 3 (1991) 3193.
- [11] J. J. P. Stewart, *Mopac 2002 Version 2.20CACHe*, Fujitsu Limited, Tokyo 2001.
- [12] <http://www.CAChSoftware.com>.
- [13] P. Matczak, S. Romanowski, *Bull. Soc. Sci. Lettres Łódź*, 54, Sér. Rech. Déform., 45 (2004)101.
- [14] Y. Waseda, K. Hirata, M. Ohtani, *High Temp. High Pressures*, 7 (1975) 221.

- [15] P. Matczak, S. Romanowski, *47 Zjazd PTChem i SITPChem, Wrocław 12-17 września 2004, Materiały Zjazdowe*, vol. 2, p. 602 (in Polish).
[16] S. Romanowski, *Pol. J. Chem.*, 67 (1993) 1709.
[17] G. E. Gdowski, J. A. Fair, R. J. Madix, *Surf. Sci.*, 127 (1983) 541.
[18] K. Balasubramanian, P. Y. Feng, *J. Chem. Phys.*, 92 (1990) 541.
[19] S. Holloway, *Surf. Sci.*, 540 (2003) 1.

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