

## Computer modelling of carbon adsorption on metal surfaces

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The research project is devoted to computer modelling of the carbon atom interactions with the transition-metal surfaces (Pd, Ni, Cu, Ag, Fe) and deactivation of the metal catalysts by carbon deposits.

The quantum calculations of the present work have been performed using the DFT method (Gaussian 98 code). In our analysis the method of the Potential Energy Surfaces (PES) has been applied. The calculations of the carbon binding energy have been performed for a large number of physically different positions (X,Y) of the C atom over the elementary cell of the metal. After correction for the energy of the separated metal cluster and C atom we obtain the map of the C atom binding energy as a function of its (X,Y) position.

The PES have been constructed for Ni, Pd, Cu, Ag and Fe. It was found that for Pd, Ni and Fe the C atom binding is very strong and the atom is trapped in the position at the cell edge. In order to remove the C atom from this position a large activation energy is required: 1.6 eV for Pd and 2.6 eV for Ni. The equilibrium distances of the C atom from the metal plane are 0 at these positions which means that the sites form the entrance channels into the metal bulk. Similar results are obtained for Fe. The results agree with the experimental findings such as the presence of the stable carbon deposits on the Pd surface and penetration of carbon into the metal bulk. In contrast, for the Cu and Ag cases the binding is much weaker and the carbon deposit can be easier removed from the surface.

Another part of the calculations concerns the binding energy of the hydrogen or oxygen atom in different positions over (a) the planar Pd<sub>5</sub> cluster and (b) the Pd<sub>5</sub> cluster with the C atom built into the plane at the cell edge. For the latter case the trapped C atom blocks the diffusion paths of the H (or O) atoms on the metal surface and, thus, hinders the surface reaction processes.

## 1. INTRODUCTION

Catalyst deactivation leads to substantial economic losses connected with necessity of the catalyst regeneration or even its replacement. Production of carbon deposits is one of numerous phenomena responsible for the deactivation during the course of catalyzed reactions. The carbon deposits frequently accompany such processes as dehydrogenation, polymerization and catalyzed decomposition of organic compounds, they result from undesirable side reactions. The deposits are composed of macromolecular hydrocarbons, both aromatic and aliphatic and may even contain elemental carbon. The hydrogen-to-carbon ratio of the deposits ranges from 2 down to almost 0. The deposits exhibit different morphology: carbon fibres both linear and spiral, graphite-like structures, etc. The forms of carbon deposits depend mostly on the rate of the deposit formation – as a rule, the faster decomposition of unsaturated hydrocarbons the lower degree of order in growing deposit [1, 2].

The carbon deposits frequently appear in the course of hydrogen decomposition processes on the metals from the transition group like Pd, Ni, Co, or Fe [3,4]. For instance it was found that the deposit growing on the surface of the Ni-Fe catalyst has the fibrous structure at the temperature 815 °C. The shape of the fibres, from linear to spiral, depends on the Ni/Fe content in bimetallic alloy. At temperatures higher than 865 °C the deposit transforms to a graphite-like structure.

Catalytic activity can be restored by interaction of deposit with gaseous oxygen, hydrogen or carbon dioxide – many technological solutions have been proposed.

The aim of the investigations presented in this paper was to gain insight into the mechanisms of blocking the catalytic processes by carbon atoms. The computer simulations both of the classical (Molecular Dynamics) and the quantum character (Quantum Chemistry and Dynamics) have been applied. The following computational projects have been completed: (1) The potential energy surfaces (PES) for binding of a carbon atom at different positions over the elementary surface cells of Pd, Ni, Cu, Ag metals and their mixtures. The optimal sites for the C atom localization over the metal surfaces have been found. (2) The Molecular Dynamics calculations of the palladium surface with adsorbed carbon atoms for different coverage of the metal surface by carbon. (3) The potential energy surfaces for interaction of the hydrogen (or oxygen) atom in contact with  $\text{CPd}_5$  cluster have been obtained. It was found that the presence of carbon atom modifies (significantly increases) the potential barriers for diffusion of the H (O) atom over the metal surface.

## 2. BINDING OF ATOMIC CARBON ON METAL SURFACES

The quantum-chemical calculations were performed using the DFT part of the Gaussian 98 [5] suite of programs. The gradient-corrected Becke functional for the exchange [6] has been applied in our calculations. We used the Perdew – 1986 correlation functional [6] and combined it with the former functional to the form of the B3P86 hybrid functional (the code words for different functionals are commonly accepted and explained, for instance, in the Koch and Holthausen book [6]). In order to check the sensitivity of the calculations to the exchange-correlation functional we repeated the calculations of the carbon binding energy to metals for the B3LYP hybrid functional [6]. We found that different functionals give the Potential Energy Surfaces with almost identical geometry. The energy surfaces are slightly (by about 0.1 eV) and almost uniformly shifted for different functionals. For all the calculations reported here the LANL2DZ basis set was used. This is the full double-zeta set [7] which includes the Los Alamos effective core potentials due to Hay and Wadt [8].

In our analysis the method of the Potential Energy Surfaces (PES) has been applied. We studied the system composed of a carbon atom and a planar  $\text{Me}_5$  metal cluster of the fcc structure ([100] surface). The internuclear distances between the metal atoms were fixed at the positions of the crystal lattice of the metal. The calculations of the carbon binding energy have been performed for a large number of physically different positions (X,Y) of the C atom over the elementary cell of the metal. The (X,Y) points were selected inside of the Dirichlet region of the central Pd atom and then the rules of symmetry of the fcc lattice were applied to cover the whole cell. Thus, outside of the central Dirichlet region the map does not correspond to the real Pd cluster but rather to the fcc lattice cell of the [100] surface. The direction along the X or Y axis was sampled at 21 evenly spaced points. For a given (X,Y) point we performed the calculations of energy of the C-metal system for different heights Z of the C atom above the metal plane and found the value of  $Z_{\text{opt}}$  that produces the lowest energy of the system. The calculations were performed for the lowest possible spin states. After correction for the energy of the separated metal cluster and C atom we obtain the three-dimensional map of the C atom binding energy as a function of its (X,Y) position. The plot of  $E_b(X,Y,Z_{\text{opt}})$  forms the Potential Energy Surface (PES).

Figure 1 shows the results of the calculations for C-Pd system using the B3P86 model. The upper part of the figure shows the three-dimensional plot of the C atom binding energy  $E_b$  as a function of the (X,Y) coordinates of the carbon atom over the Pd surface cell. The unit X, Y of coordinates is 1.945 Å. The PES shows interesting information. The weakest binding of the C atom appears exactly “on top” of the Pd atom, -6.08 eV. The “on bridge” position is

characterized by a stronger binding,  $-7.75$  eV, but the lowest energy position on PES (the highest binding energy) is situated at the cell edge, directly above the Pd atom from the subsurface layer,  $-9.36$  eV. The C atom is practically immobilized at this site. In order to move from one such site to another the atom has to cross a potential barrier of about  $1.6$  eV. The conclusion about the C-binding site was verified by the calculation of the PES for two Pd layers.

## C-Pd<sub>5</sub>

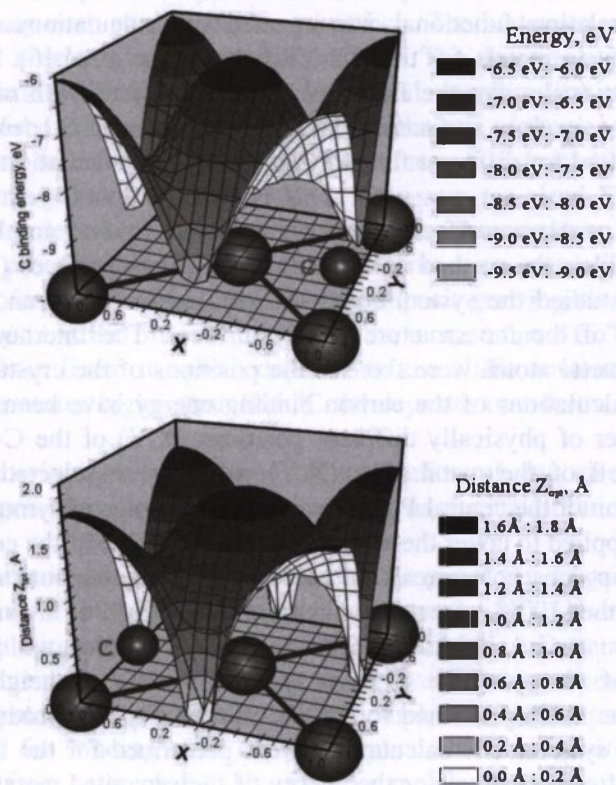


Fig. 1. (Upper part) Three-dimensional plot of the binding energy of a single C atom in different positions over the elementary surface cell (fcc [100]) of palladium. Positions of Pd atoms are indicated in the Figure. (Lower part) A 3-D plot of the optimized distance of a C atom from the metal surface in different positions over the Pd cell,  $Z_{opt}$ . The unit on the X and Y axis is  $1.945$  Å. The color coding of the energy and the distance scale is given in the Figure. The calculations have been performed by the DFT/B3P86 method.

The optimum distance  $Z$  of the C atom from the Pd plane (lower part of Figure 1) varies quite significantly over the positions in the cell. The “on top” position ( $X=0$ ,  $Y=0$ ) is characterized by relatively large distance  $Z=1.74 \text{ \AA}$ . The “on bridge” position ( $X=0.5$ ,  $Y=0.5$ ) shows a shorter distance  $Z=1.25 \text{ \AA}$ . The movement of the C atom from the “on bridge” point along the  $Y=1-X$  line towards the cell edge is characterized by a steady decrease of the  $Z$  distance. In the vicinity of the cell edge (at the top of the barrier,  $X=0$ ,  $Y=1$ ) the  $Z$  distance falls down to  $0 \text{ \AA}$  and the C atom builds-in into the metal surface. The C atom, can then choose one of the two possible paths: either to migrate over the surface crossing a high barrier, which is rather improbable, or migrate under the surface down from the entrance at this site.

Similar plots of the PES have been constructed for Ni, Pd, Cu and Ag clusters and for the mixed clusters. The results for the neat metals are shown in Figure 2. The same scale of energy has been used for all the plots. It was found that for Pd and Ni the C atom binding is very strong (binding energy exceeds 9 eV) and the atom is trapped in the position at the cell edge. In order to remove the C atom from this position a large activation energy is required, about 1.6 eV for Pd and 2.6 eV for Ni. The equilibrium distances at these positions are 0 which means that the sites form the entrance channels into the metal bulk. The results agree with the experimental findings such as the presence of the stable carbon deposits on the Pd surface and penetration of carbon into the metal bulk [1,2]. In contrast with Pd and Ni, in the Cu and Ag cases the binding is much weaker (between 3 and 5 eV). The PES's are rather flat and the carbon deposit can be easier moved over the surface – the activation energy necessary to remove the C atom from its equilibrium position is of the order of 0.54 eV for Cu and 0.4 eV for Ag. The equilibrium positions of the C atoms are 0.8 and 1  $\text{\AA}$  above the metal plane for Cu and Ag, respectively. The adsorbed carbon atoms are more exposed to interaction with other atoms and molecules and the deposit is easier to remove.

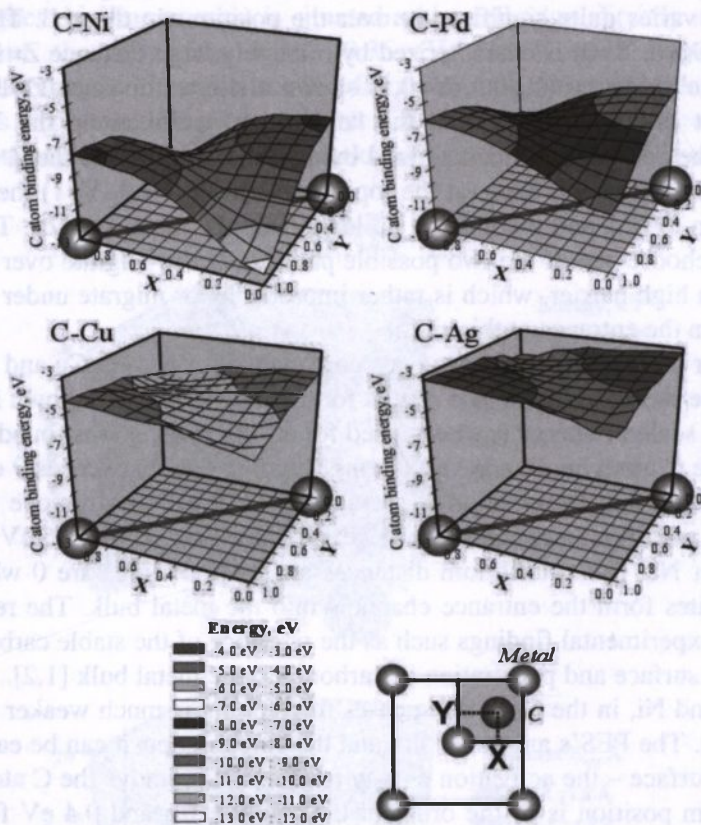


Fig. 2. The binding energy of the C atom in contact with the metal surfaces. The plots for the upper right quarter of the surface cell are shown. The upper left plot shows the PES for Ni, upper right for Pd, lower left for Cu and lower right for Ag.

Figure 3 shows an example of the PES for C atom interacting with the following metal clusters simulating palladium silver alloys: Pd<sub>5</sub> (upper left), Pd<sub>4</sub>Ag (upper right), PdAg<sub>4</sub> (lower right) and Ag<sub>5</sub> (lower left).

For the Pd cell the lowest energy (-9.4 eV) of the adsorbed C atom appears at the edge of the Pd surface cell. The trapping site forms an entrance for the C atom under the surface of the metal structure. Addition of the Ag atoms changes dramatically the PES towards weaker binding of the C atom to the surface. The PES for the PdAg<sub>4</sub> cell has different geometry with the single minimum at the top of the Pd atoms, while the pure Ag cell shows the binding energies between 3 and 4 eV with no definite trapping sites for the C atom.

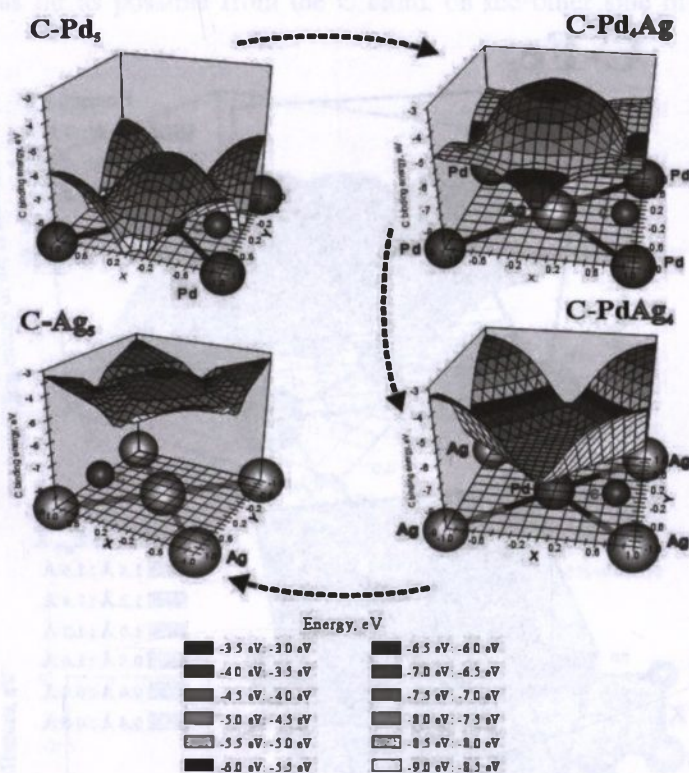


Fig. 3. Potential energy surfaces for C atom in different positions (X,Y) over the following metal clusters: Pd<sub>5</sub> (upper left), Pd<sub>4</sub>Ag (upper right), PdAg<sub>4</sub> (lower right) and Ag<sub>5</sub> (lower left). For a given (X,Y) the vertical distance Z was optimized with respect to the binding energy E<sub>b</sub>. The unit of the X, Y axis is 1.945 Å for upper figures and 2.045 Å for lower figures.

Figure 4 shows the PES for C atom interacting with the iron surface (upper part), the lower part of the Figure shows the optimized distance  $Z_{\text{opt}}$  as a function of the position (X,Y) over the cell. For the bcc surface Fe cell the lowest energy of the adsorbed C atom appears at the centre of the cell. The binding energy is very high, of the order of 9 eV. However, in contrast with the Pd and Ni cases, in order to move the C atom from this position to the neighbouring cell one has to overcome the barrier of the order of only 0.4 eV. The equilibrium distance of the C atom from Fe surface at the trapping site (the centre of the cell) is very small, 0.39 Å, and the trapping site forms an entrance channel for the C atom under the surface of the metal structure.

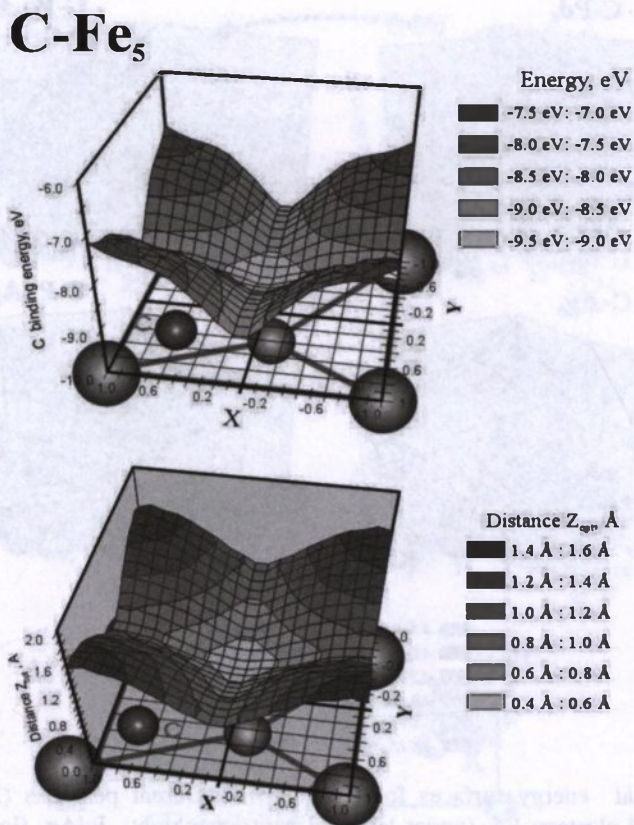


Fig. 4. Upper : Potential energy surfaces for C atom in different positions (X,Y) over Fe<sub>5</sub> bcc [100] surface cell. Lower: Optimized distance  $Z_{opt}$  as a function of (X,Y). The unit of the X, Y axis is 2.87 Å, the nearest neighbour distance is 2.485 Å.

### 3. BINDING OF THE H AND O ATOMS ON METAL SURFACES WITH ADSORBED CARBON ATOMS

Another part of the calculations concerns the binding energy of the hydrogen or oxygen atom in different positions over (1) the planar Pd<sub>5</sub> cluster and (2) the Pd<sub>5</sub> cluster with the C atom built into the plane at the cell edge.

Figures 5 and 6 show in upper parts the binding energy surfaces of the H atom (Figure 5) and the O atom (Figure 6) placed over the CPd<sub>5</sub> cluster. The position of the C atom corresponds to the energy minimum shown in Figure 1 the centre of the cell edge and  $Z=0$ . Figure 5 shows that the lowest energy of the



H atom is as far as possible from the C atom, on the other side of the Pd-Pd bond.

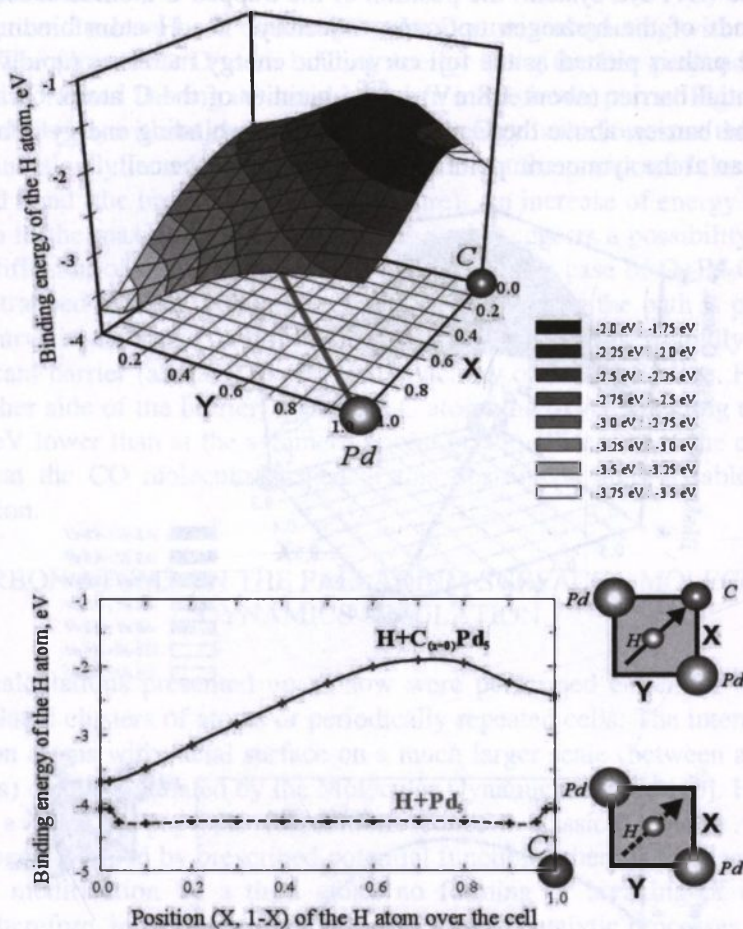


Fig. 5. Upper part: Three-dimensional plot of the binding energy surface for the H atom in different positions (X,Y) over Pd<sub>5</sub>C cluster. Lower part: The plots of the binding energy of the H atom in contact with the Pd<sub>5</sub> (broken curve) and Pd<sub>5</sub>C (full curve) clusters. The binding energy is plotted along the axis perpendicular to the Pd-Pd bond and drawn through the centre of the bond,  $Y=1-X$ , as indicated in the right figure. The X and Y unit is 1.945 Å.

The plot of the H atom binding energy along the line perpendicular to the Pd-Pd bond and halving the bond is shown in the lower part of Figure 5. For the former case (H+Pd<sub>5</sub> without carbon) we have found [9] that the H atom energy is the lowest along the line and the energy curve is almost flat (the broken curve in

the Figure). A small increase of energy (0.17 eV) appears at the ends of the Pd cell. This suggests a possibility of easy surface diffusion along the path. For the latter case (H+Pd<sub>5</sub>C system) the position of the trapped C atom is exactly at one of the ends of the hydrogen optimum trajectory. The H atom binding energy along the path is plotted as the full curve. The energy increases rapidly forming a substantial barrier (about 1.8 eV) in the vicinity of the C atom. On the other side of the barrier, above the C atom, the hydrogen binding energy is by 0.5 eV higher than at the symmetric point on the other side of the cell.

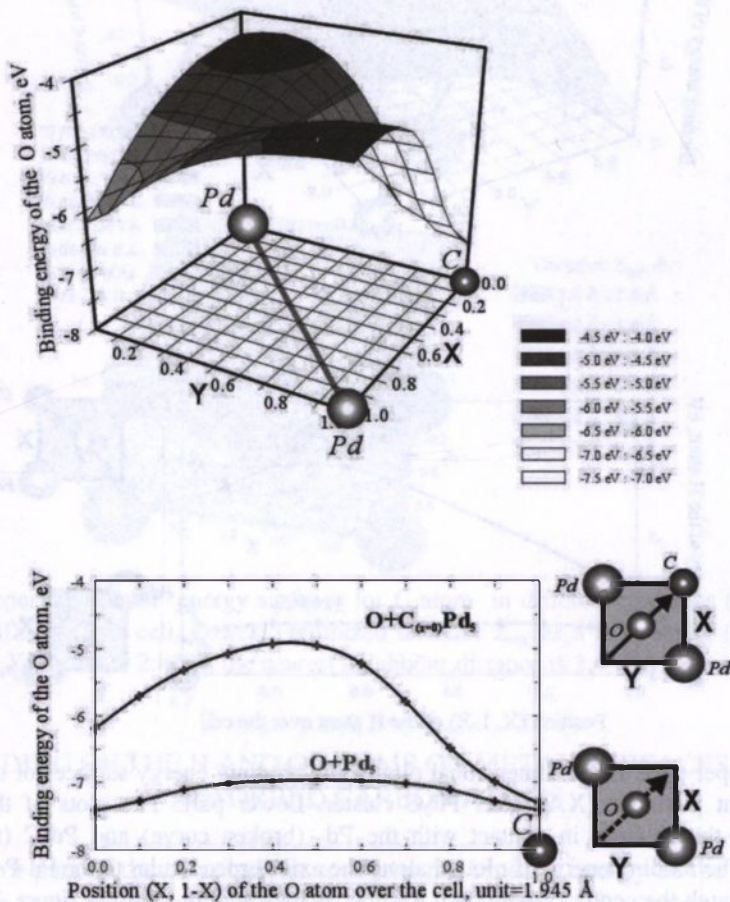


Fig. 6. Upper part: Three-dimensional plot of the binding energy surface for the O atom in different positions (X,Y) over Pd<sub>5</sub>C cluster. Lower part: The plots of the binding energy of the O atom in contact with the Pd<sub>5</sub> (broken curve) and Pd<sub>5</sub>C (full curve) clusters. The binding energy is plotted along the axis perpendicular to the Pd-Pd bond and drawn through the centre of the bond,  $Y=1-X$ , as indicated in the right figure. The X and Y unit is 1.945 Å.

A possible interpretation of the results is that the carbon atom blocks the diffusion paths of the H atoms on the metal surface and, thus, hinders the surface reaction processes.

Similar results have been obtained for the O atoms interacting with the Pd<sub>5</sub>C clusters. The plot of the O atom binding energy along the line perpendicular to the Pd-Pd bond and halving the bond is shown in the lower part of Figure 6. For the case of O+Pd<sub>5</sub> without carbon, the O atom energy is the lowest at the edge of the cell and slowly increases towards a maximum at the position of the O above the Pd-Pd bond (the broken curve in the Figure). An increase of energy from the minimum to the maximum is 0.45 eV. This again suggests a possibility of easy surface diffusion of the O atom along the path. For the case of O+Pd<sub>5</sub>C system with the trapped C atom the O atom binding energy along the path is plotted as the full curve in the lower part of Figure 6. The energy increases rapidly forming a significant barrier (about 1.26 eV) in the vicinity of the Pd-Pd line. However, on the other side of the barrier, above the C atom, the oxygen binding energy is by 1.26 eV lower than at the symmetric point on the other side of the cell. This means that the CO molecule formed at this position is highly stable against dissociation.

#### 4. CARBON ATOMS ON THE PALLADIUM SURFACE – MOLECULAR DYNAMICS SIMULATION

The calculations presented up to now were performed either for relatively small isolated clusters of atoms or periodically repeated cells. The interaction of the carbon atoms with metal surface on a much larger scale (between a 10<sup>3</sup> and 10<sup>4</sup> atoms) can be simulated by the Molecular Dynamics method [10]. However, there is a price to pay: the calculations concern classical objects with the interactions described by prescribed potential functions, there is no electrons, no potential modification by a third atom, no forming or breaking of chemical bonds. Therefore, in the theoretical investigations of catalytic processes, the MD calculations can only be of an auxiliary character.

The MD simulations of the palladium surface for different coverages of the surface by the carbon deposits have been performed. The lowest coverage corresponded to about 100 C atoms per 450 Pd atoms on the surface, the higher coverage calculations involved 200, 400, 500 and 800 C atoms. For the former case we observe full dispersion of the C atoms on the metal surface. At the higher coverages, the initially adsorbed C atoms behave like nucleation centers: most of the later arrivals prefer binding to the already adsorbed C atoms than to metal atoms and form the carbon clusters built-in into the surface. The simulations show a possibility of the carbon diffusion deep into the metal structure for the Pd and Ni cases. The carbon atoms remaining on the surface

form quasi-linear clusters that may be precursors of the different spiral forms and carbon fibres observed in microscopic pictures of the carbon deposits. Some results are shown in Figure 7 for 507 C atoms on the surface of 10 x 450 Pd slab. The top view of the surface and a vertical crosssection are presented and they prove the C atom cluster forming and relatively deep diffusion of carbon under the palladium surface.

**MD Simulation:  
507 C atoms on 4500 Pd atoms (10 layers)**

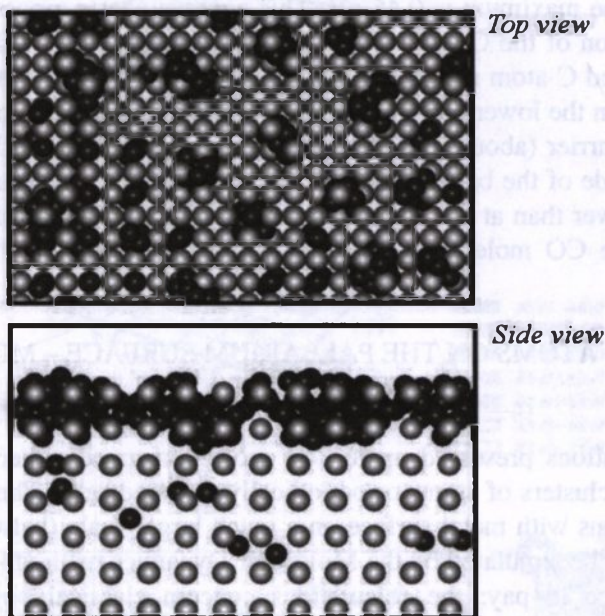


Fig. 7. Snapshots of the Molecular Dynamics simulation of the Pd [100] surface of the 10 x 450 Pd slab covered with 507 carbon atoms. The upper part shows the top view, the lower part the vertical crosssection of the simulation box.

## 5. CONCLUSIONS

A possible interpretation of the results is that the carbon atom, which is built into the palladium surface, blocks the diffusion paths of the H atoms or O atoms in its vicinity and, thus, it slows down some surface diffusion processes. As a consequence, the catalytic processes involving the mobile H or O atoms are hindered and, in macro scale, we observe loss of the catalyst activity.

## 6. REFERENCES

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