Materials Science-Poland, Vol. 24, No. 2/2, 2006

Hydrogen atoms at the palladium surface, at the MgO surface and at the Pd–MgO metal-support boundary. Towards computer modelling of the spillover effect

W. M. BARTCZAK, J. STAWOWSKA*

Institute of Applied Radiation Chemistry, Technical University of Łódź,
ul. Wróblewskiego 15, 93-590 Łódź, Poland

The work is devoted to computer modelling of interactions of atomic hydrogen with palladium and MgO surfaces, and with Pd atoms adsorbed on MgO surface. Quantum calculations were performed using the methods of the Density Functional Theory (DFT) with gradient-corrected functionals for electron exchange and correlation. The potential energy surfaces were calculated for a hydrogen atom interacting with Pd and MgO surfaces. The results indicate an easy (0.17 eV activation barrier) diffusion of hydrogen atoms over the metal surface. A possibility of migration of H atoms from the metal surface onto the MgO support surface (the "spillover effect") is discussed. It was found that the transfer of a hydrogen atom from the vicinity of a Pd atom to O sites of the MgO surface results in the energy gain of the order of 0.5 eV. The transfer, however, is an activated process with the activation energy about 0.8 eV.

Key words: *hydrogen; palladium; MgO; surface diffusion; catalysis; spillover*

1. Introduction

An important model of catalysis is represented by the behaviour of the simplest molecule, H_2, dissociating on surfaces of transition and noble metals, and their alloys. Subsequent migration of atomic hydrogen over the metal surface and possible migration to a different phase (support) provide a classical definition of the "spillover effect" [1].

Metal particles supported on oxides make an important group of catalysts in the heterogeneous catalysis. The active phase is composed of a transition or noble metal, simple metal oxides being selected for the support phase. Magnesium oxide is frequently selected due to its favourable thermal and mechanical properties.

The literature on catalysis contains a large number of papers on the H atom interaction with metals, mostly Pd, Pt, Ni, Ag and Cu. The book [2] contains a useful review of early theoretical work, and is still worth revisiting, in spite of a large number

---

*Corresponding author, e-mail: joannas@mitr.p.lodz.pl

of theoretical papers on the topic. Calculations of electronic properties of transition metals performed by traditional *ab initio* methods were not very successful. Salahub, Morokuma and other authors advocated the use of the density functional theory (DFT) rather than the classical Hartree–Fock scheme. There exists a large number of review papers and compilations on this topic and the proceedings of a recent ACS Symposium [3] can serve as a source of references. A significant progress in the transition-metal calculations is connected with the “gradient-corrected” density functionals, sometimes referred to as non-local functionals [4].

Recent years brought a continuous stream of papers devoted to the problem of hydrogen adsorption on metals, in particular on palladium. Numerous references and a detailed treatment of hydrogen interaction with Pd have also been given in the recent book by Gross [5] and in the review paper by Efremenko [6]. A number of authors applied the DFT method with local density approximation and generalized gradient approximation (GGA) and with periodic boundary conditions. For instance Paul and Sautet [7], and Løvvik and Olsen [8] investigated adsorption of atomic hydrogen on the palladium [111] surface. GGA calculations are also presented in the papers by Dong and Hafner [9], Ledentu et al. [10], and Dong et al. [11]. Okuyama et al. [12] performed a detailed experimental investigation of hydrogen adsorption at Pd [100] surface and penetration into the bulk of Pd.

Interaction of metals with the MgO surface was the subject of numerous theoretical and experimental papers [13–19]. Metals like Ni, Pd, Pt, W form relatively strong covalent bonds with the MgO surface with the binding energy of the order of 1 eV per metal atom, oxygen sites of the MgO lattice making preferred metal positions. Calculations of the interaction of Pd with MgO reported in [20] predict the binding energy on top of the O site to be 1.35 eV and the distance from the O site equal to 2.11 Å. The binding energy of Pd on top of the Mg site is only 0.43 eV. Giordano et al. [17] performed calculations of Pd deposit on the MgO surface and found a favourable adsorption of Pd over the oxygen vacancies. Vervish and coworkers [18] applied the *ab initio* quantum chemical calculations and second moment approximation to analyse the development of the structure of larger Pd clusters on MgO surface.

In contrast to numerous studies of metal adsorption on the MgO surface, we are unaware of any recent quantum calculations which consider the transfer of atomic hydrogen to the surface of support which is the basis for the spillover phenomenon. Therefore, the aim of the present work is to investigate interactions of the atomic hydrogen with the surface of MgO and particularly the interactions with the MgO surface containing adsorbed Pd atoms, and to investigate a possibility of the transfer of hydrogen atoms from the metal onto the MgO surface.

2. Method of calculations

The quantum-chemical calculations were performed using the DFT part of the Gaussian98 [21] suite of programs. The gradient-corrected Becke functional for the exchange [4] has been applied in our calculations. We used the Perdew-1986 correlation functional [4] 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, by Koch and Holthausen [4]). However, in order to check the sensitivity of the calculations to the exchange–correlation functional, we performed calculations of the hydrogen binding energy to metals and to MgO for the B3LYP and B3PW91 hybrid functionals and the standard BP86 functional [4]. We found that various functionals give potential energy surfaces with almost identical geometries, though the energy surfaces are slightly shifted for different methods. As a rule, we obtained the highest energy values for the BP86 functional, and lower values for B3LYP and B3PW91. However, the differences between the highest and lowest energy values for the series of functionals are within the range of 0.1 eV. Slightly lower values (by another 0.1 eV) were obtained for the B3P86 functional. Positive features of the latter functional were the stability and a relatively fast convergence of the calculations, thus we decided to use it as a standard functional for our calculations.

For all the calculations reported here, the LANL2DZ basis set was used. This is a full double-zeta set [22] which includes the Los Alamos effective core potentials due to Hay and Wadt [23]. The BSSE correction was calculated for the H atom interaction with the Pd_5 cluster (full energy surface) and with the $(MgO)_8$ cluster. We found that the correction leads to a uniform shift of the binding energy surfaces by about 0.1 eV. Differences of the H atom energy for different positions over the cluster are not affected by the BSSE correction. As the computational cost of the calculation of the potential energy surfaces with BSSE is very high, and the correction does not change the potential barrier heights for the H atom movement, we decided to neglect it in the very time-consuming calculations of the H atom transfer from metal to MgO.

In the first part of the calculations, we studied the system composed of a hydrogen atom and a planar $Metal_5$ 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 have been performed for a large number of physically different positions (X,Y) of the H atom over the metal cluster. 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 the central Dirichlet region the map does not correspond to a real Pd cluster but rather to an *fcc* lattice cell of the [100] surface. For a given (X,Y) point we performed calculations of the energy of H–$Metal_5$ system for different heights Z of the H atom above the metal plane and found an optimum value (Z_{opt}) yielding the lowest energy of the system. The calculations were performed for the lowest possible spin states. After subtraction of the energies of the separated $Metal_5$ cluster and H atom we obtain a three-dimensional plot of the H atom binding energy as a function of its (X,Y) position. The plot of $E_b(X,Y,Z_{opt})$ forms the potential energy surface (PES).

In the calculations concerning MgO surface, on account of the ionic character of the MgO matrix, we checked very carefully the influence of distant ions on the H atom binding energy. Since calculations employing periodic boundary conditions have a strong drawback of replicating adsorbed atoms and also impose an artificial layer structure on the system, we selected another way of calculations. A bound hydrogen atom carries rather small fractional charge: from –0.04*e* at the Mg sites to about 0.2*e* in the vicinity of the O sites and the H polarizability is very small, of the order of 6.6×10^{-31} m^3. This allows us to expect rather small influence of the distant ions on the H atom binding energy. To include the effect of the MgO ionic lattice we surrounded the cluster with the point charges. The calculations repeated for increasing number of point charges show that the system of (12×12 charges in a single layer)×4 layers is large enough to ensure the convergence of the binding energy.

We performed a series of calculations of a large MgO cluster and found the following charges on the Mg and O sites for different definitions of the atomic charge: 1) for the Mulliken definition the charges on O sites were between –0.91*e* and –1.18*e*, on Mg sites between 0.96*e* and 1.3*e*; 2) for the Breneman and Wiberg definition of the charges fitted to electrostatic potential [21] the O sites were charged between –1.24*e* and –1.44*e*, the Mg sites between 1.29*e* and 1.43*e*; 3) for the Merz–Singh–Kollman definition [21] the O sites had charges between –1.3*e* and –1.57*e* and the Mg sites between 1.35*e* and 1.57*e*. Hence we assumed the unit values of the point charges, rather than the nominal ±2*e*. Thus, the total number of point charges included into the $(MgO)_6$ cluster calculations was 564. It appears that for the hydrogen atom the contribution is negligible, of the order of 0.01 eV in most of the (X,Y) points. The contribution scales linearly with the assumed site charge and, therefore, it is also negligible for the ±2*e* charges.

3. Results and discussion

3.1. Interaction of hydrogen with palladium surface

Figure 1 shows results of the calculations for the H–Pd system performed using the B3P86 model. The upper part of the figure shows a three-dimensional plot of the H atom binding energy E_b as a function of the (X,Y) coordinates of the hydrogen atom over the Pd surface cell. The unit X, Y of coordinates is 1.945 Å. On the energy surface of Figure 1 we observe a deep valley (marked white and very light grey) where the H atom binding energy is much lower than anywhere else in the cell. The valley is perpendicular to the Pd–Pd bonds and halves the bond. The cross-section of the energy surface along the direction $Y = 1 - X$ perpendicular to the bond is given in Figure 2 together with the plots for different DFT versions and functionals.

The range of the coordinate in the cell is $-1 \le X \le 1$. From $X = 0.5$ (over the Pd–Pd bond centre) up to $X = 0.96$ (or to 0.04 in the other direction) the energy is practically constant. A slight variation in energy, of the order of 0.01 eV, is certainly below the accuracy of the calculations. Between $X = 0.96$ and $X = 1$ (or between $X = 0.04$ and $X = 0$) the energy slightly increases, by about 0.17 eV. Crossing this barrier means that the H atom is transferred to another surface cell. Hence, the barrier along the line *Y* = 1 – *X* can be interpreted as the activation barrier for a diffusive movement of the H atoms over the surface of palladium. The activation energy for the H atom diffusive motion at the surface is about 0.17 eV, i.e. 3.9 kcal/mol with the barrier width about 0.08 Å. Both the thermal mechanism and quantum-mechanical tunnelling give very significant probability of the barrier crossing.

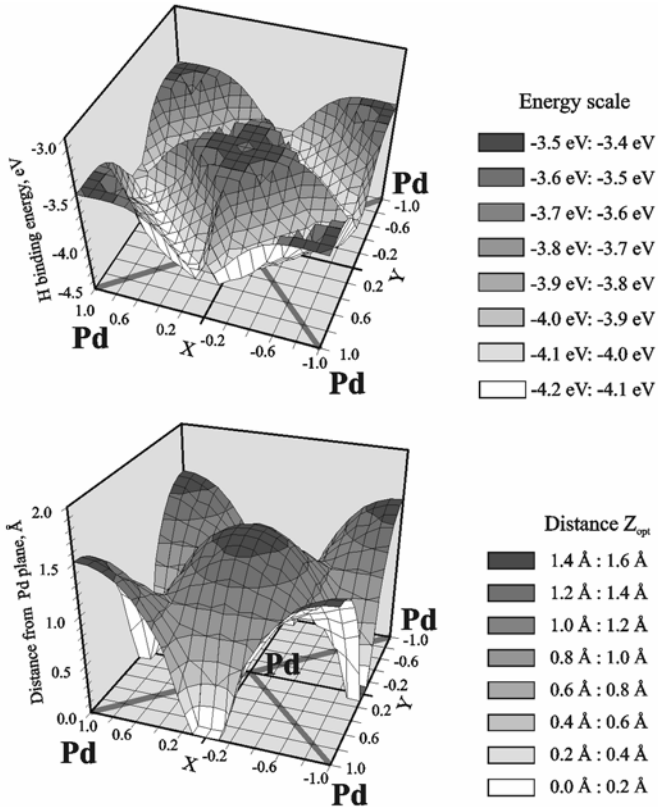


Fig. 1. Upper figure: 3-D plot of the binding energy of a single H atom in different positions over the elementary surface cell (*fcc* [100]) of palladium. Lower figure: a 3-D plot of the optimized distance of a H atom over the Pd cell, Z_{opt}. The unit on the *X* and *Y* axis is 1.945 Å. The coding 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 H atom from the Pd plane (lower part of Fig. 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 = 1.52 Å. The „on bridge" position (*X* = 0.5, *Y* = 0.5) shows a shorter distance Z = 0.98 Å. The movement of the H 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 Å. This means that at the foot of the barrier the H atom, which is placed very close to the Pd surface plane, can choose one of the two possible paths: either migrate at the surface crossing the barrier of about 4.0 kcal/mol or migrate under the surface with a similar barrier.

Okuyama et al. [12] estimated the barrier for the subsurface diffusion of the H atom to be ca. 1.1 kcal/mol. Paul and Sautet [7], in their calculations of the hydrogen adsorption on the Pd [111] surface, give somewhat different values. They obtained 7.6 kcal/mol for the subsurface penetration and roughly estimate 3.5 kcal/mol for the surface diffusion. Due to very low barriers, both paths are possible. Finally, it is worth mentioning that our result for the activation barrier for surface diffusion is very close to the measured activation energy of the H atom bulk diffusion in Pd which is 5.3 kcal/mol [24].

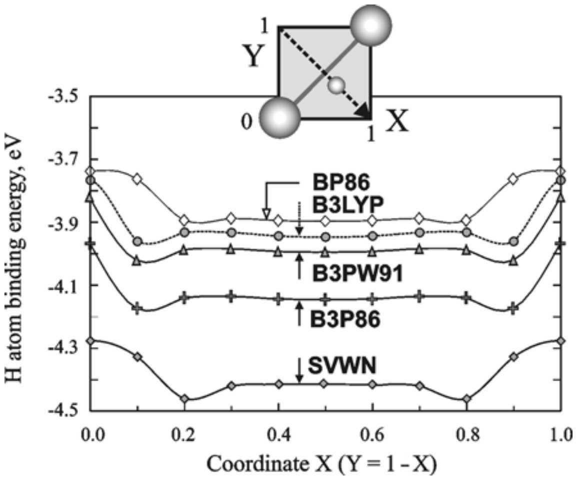


Fig. 2. Comparison of the H atom binding energy along the direction $Y = 1 - X$ (perpendicular to the Pd–Pd bond) in a unit Pd cell. X axis unit corresponds to 1.945 Å. The calculations were performed using the DFT method with the exchange-correlation functionals as labelled in the figure

The binding energy for hydrogen atom as predicted by different DFT models is shown in Figure 2. The figure shows the results for the DFT calculations with gradient-corrected hybrid functionals: B3P86, B3PW91 and B3LYP, for gradient-corrected DFT with the “pure” BP86 functional and for the local DFT with the SVWN (combination of the Slater exchange and Vosko–Wilk–Nusair correlation [4]) functional. The values of the binding energy and the geometry of the surface are slightly different for different methods, but for all the PES surfaces we observe a flat valley perpendicular to the Pd–Pd bond ($Y = 1 - X$) ending with low and narrow energy barrier.

In Figure 2 we compare the energy variation along the line $Y = 1 - X$ for different computational models. The different methods result in the shift of the energy plateau at the bottom of the valley but the height of the barrier is roughly the same, of the order of 0.2–0.3 eV. It is interesting to note that the hybrid functionals predict more narrow barrier than the remaining two functionals. More results are given in [25]. However, the general conclusion holds for all the models: the valley $Y = 1 - X$ and its symmetric counterparts provide an easy diffusion path for atomic hydrogen on the palladium surface, the path ends at the edge of the Pd cell providing channels for the H atom penetration beneath the metal surface.

3.2. Calculations of the energy surface for an H atom interacting with MgO clusters

Figure 3 shows the energy surface for the H atom interacting with the MgO surface. A cluster of 8 MgO pairs in the single layer was used in the calculations, its geometry being that of the surface of the MgO crystal (*fcc* [100] structure). The cluster was embedded into the system of four layers of point charges described in the previous section, 560 charges altogether. The calculations have been performed for

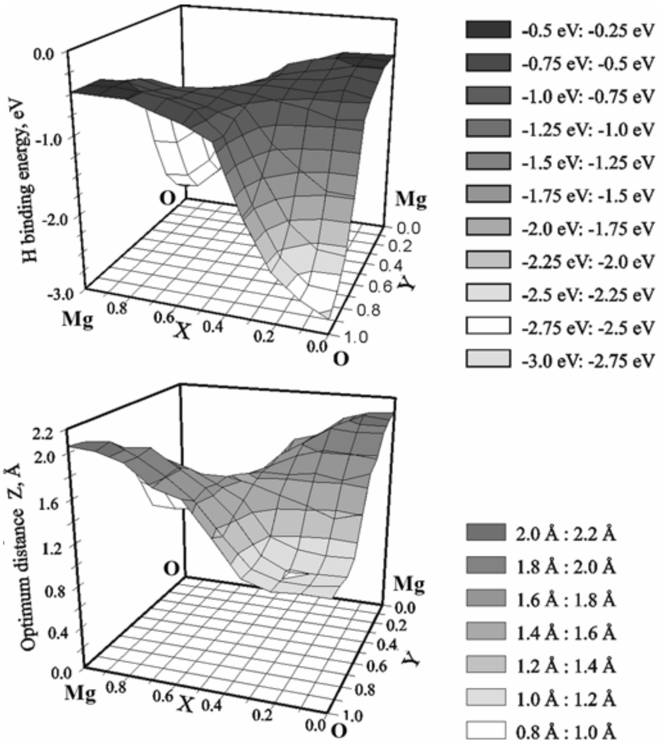


Fig. 3. Upper figure: a 3-D plot of the binding energy surface of a H atom in different positions over (MgO)$_8$ cluster surrounded by point charges. For a given position (X,Y) over the MgO cell the distance Z of the H atom from the MgO plane was optimised in order to obtain the highest binding energy. The unit on the X and Y axis is 2.106 Å. Lower figure: the optimum distance Z of the H atom as a function of (X,Y)

a large number of physically different positions (*X*,*Y*) of the H atom over the MgO square and then the rules of symmetry of the *fcc* lattice were applied to cover the whole cell. For a given (*X*,*Y*) point we performed the calculations of the energy of H–$(MgO)_8$ system for several heights Z of the H atom above the MgO plane and found the value of Z_{opt} that yields the lowest energy of the system. The binding energy of H atom was calculated as a difference of the total energy of the $H(MgO)_8$ cluster and and the sum of energies of the separate H atom and $(MgO)_8$ cluster.

The analysis of the surface points to large energy differences between different places in the MgO cell. The energetically favourable place for the H atom is over the O^{2-} ion, the binding energy being about –2.79 eV. It is interesting to note that the region of the lowest energy is near the oxygen site, the energy profile over the remaining part of the cell being rather flat. In the central region of the cell, the H binding energy is about –0.7 eV and at the Mg site increases up to –0.47 eV. The shape of the energy surface rules out the possibility of an easy migration of the H atom over the MgO surface. The potential barrier along the oxygen-oxygen line is about 2.11 eV. We cannot exclude, however, jumps to the neighbouring oxygen sites either by the over-barrier mode (catalytic processes frequently proceed at rather high temperatures which makes activated jumps rather easy) or by the under-barrier (tunnelling) mode even at lower temperatures.

The lower part of Figure 1 shows optimized distances of the H atom from the MgO plane. The largest distance corresponds to the H atom over the Mg site (2.1 Å), at the cell centre the distance is about 1.7 Å, the distance at the O sites is only about 1.0 Å. The shortest distance of the adsorbed hydrogen from the MgO plane, 0.7 Å, appears on the diagonal line connecting the O sites, roughly halfway between the O site and the cell centre.

The fractional charge of H is 0.36*e* directly above the oxygen site and about 0.3*e* in its vicinity. When the (*X*,*Y*) point is removed from the O site by more than 0.3 unit, the fractional charge decreases to almost 0. The small values of the fractional charge prevail over about 80% of the surface of the cell. Directly above the Mg site, the H charge is –0.05*e*. The small values of the hydrogen charge suggest rather negligible influence of distant ions. The correction to the H atom binding energy that results from the presence of the point charges surrounding the MgO cluster is of the order of 0.01 eV with the exception of the position directly over the O site where the energy increases sharply to about 0.03 eV.

3.3. Calculations of the energy surface for H atom interacting with Pd-MgO clusters

A substantial part of our work was focused on explaining the transport of a hydrogen atom from metal (Pd, Ni) to the MgO support. The results for Pd are given in Figures 4 and 5. Figure 4 shows the potential energy surface for the H atom interacting with the $Pd(MgO)_6$ system. The Pd atom has been placed over one of the O sites, at a distance of 2.1 Å between the nuclei. This value results from separate optimisation runs in which the Pd atom was placed at different positions over the MgO surface. The structure with the lowest energy corresponds to the Pd atom over the O site in the lattice. The geometry of the cluster is shown in the lower part of the figure. Similarly as for the previous calculations of H–MgO, the cluster was surrounded by a system of point charges.

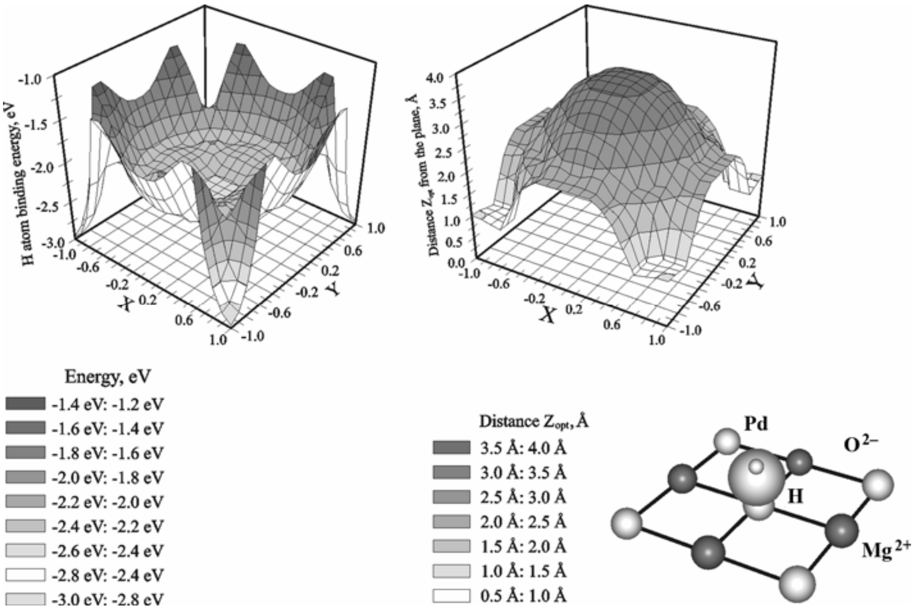
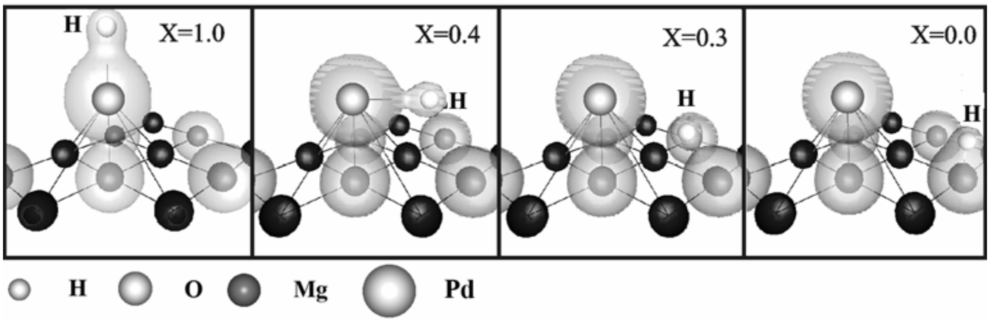


Fig. 4. Left figure: the energy surface for the H atom binding in different positions over the MgO cell with adsorbed Pd atom. The Pd atom is placed over one of the oxygen sites in the MgO lattice at the height of 2.1 Å. The H–Pd(MgO)$_6$ cluster is surrounded by the system of 12×12×4 point charges. The unit on the *X* and *Y* axes is 2.106 Å. Right figure: the optimum distance *Z* of the hydrogen atom from the MgO plane as a function of the position (*X*,*Y*) over the MgO cell. The geometry of the system is shown in the lower part of the figure

The left figure shows the energy surface. It appears that the hydrogen binding energy has a local minimum of –2.5 eV for the position of the H atom directly above the adsorbed Pd atom. The minimum is surrounded by a flat, roughly circular region with the radius of ca. 1 Å and with energy between –2.4 eV and –2.2 eV. When the H atom is shifted along the O(Pd)-O axis from the position on the top of Pd to the nearest O site, it has to cross two potential barriers: the lower one of 0.2 eV and the higher one of 0.6 eV and of 0.4 Å width. The profile of the binding energy along the O-O axis is shown in Figure 4. Beyond the second barrier, we observe a rapid decrease of the H atom energy down to –3 eV as compared with –2.4 eV on the top of Pd and –2.6 eV in the vicinity of Pd. We conclude that the H atom initially adsorbed at the metal site can be transferred to the O site of the MgO lattice with the energy gain of ca. 0.4 eV. The right part of the figure shows the optimized distance of the H atom as a function of the position (*X*,*Y*) over the MgO cell.



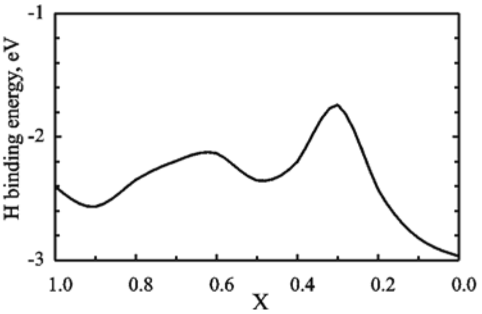


Fig. 5. Upper part: isosurfaces of the electron density ($\rho = 0.08$ *e*/Å^2) for the H–Pd(MgO)$_6$ cluster with H atom in different positions along the O(Pd)–O diagonal. The positions of the Mg, O and Pd, H atoms are marked as small grey spheres. Lower part: the H atom binding energy to the Pd(MgO)$_6$ cluster along the diagonal in the MgO cell

Figure 5 gives more information about the H atom transfer. The lower part of the figure shows the binding energy profile of a hydrogen atom along the line from the O/Pd site with the adsorbed Pd atom to the nearest O site in the MgO lattice. The energy is shown as a function of the X component of the translation vector (X, Y = X), with $X = 1$ corresponding to the O/Pd position and $X = 0$ to the O site. The upper part of the figure shows isosurfaces of the electron density for $\rho = 0.08$ *e*/Å^2 as the gray shaded regions. The small spheres indicate the positions of the O, Mg and Pd atoms. The plot for $X = 1$ shows the electron density distribution for the H atom adsorbed on top of Pd atom. The high density bridge (chemical bond) suggests localized, covalent bond between Pd and H. The plot for $X = 0.4$ shows the density distribution for the base of the high potential barrier. The H atom is directed towards the O site, the H–Pd bond is weaker but not completely broken. The plot for $X = 0.3$ shows the density distribution for the top of the potential barrier, i.e. the transition state. The H–Pd bond is already broken (energy demand) but the H–O bond is not formed due to a large distance between the reacting centres. The last plot for $X = 1$ shows the final state with the strong H–O bond (high density bridge between H and O). The plots imply that the energy barrier in the process of the H atom transfer from Pd to the O site results from the necessity of a prior breaking of the H–Pd bond without any energy compensation from the newly forming H–O bond. The H atom transfer results in the translation by about 4.1 Å: 2.97 Å in the horizontal direction and 2.8 Å in the vertical direction. The distance is very large on the scale of the chemical bonds; this explains why the H–Pd bond must be completely broken first (energy demand) and then, after a further translation the H–O bond can be formed (energy gain). Thus, the transition state may be interpreted as a state in which the H–Pd bond is already broken and the H–O bond is only beginning to form.

Summarizing, our calculations of the H atom transfer from palladium to the MgO support surface result in the conclusion that the H atom transfer is energetically favourable. The excess energy is not very large and can be roughly estimated as 0.5 eV. This finding is essential for the possibility of the inverse spillover effect which has also been observed in experiments – the hydrogen atom comes back to the metal island. The existence of potential barriers for the spillover transition makes the phenomenon sensitive to temperature. However, in order to arrive at more quantitative conclusions more computational effort is required. This work is currently performed in our laboratory.

The hydrogen atoms are trapped around the metal island, in the vicinity of the O site. This finding is essential for the possibility of the surface reactions: the phase boundary around the metal island collects the H atoms which spillover from the metal catalyst and makes the stage for numerous surface reactions.

References

[1] *Spillover of Adsorbed Species* G.M. Pajonk, S.J. Teichner, J.E. Germain (Eds.), Elsevier, Amsterdam, 1983.
[2] Yoshida S., Sakaki S., Kobayashi H., *Electronic Processes in Catalysis*, Wiley-VCH, New York, 1994.
[3] *Transition State Modeling for Catalysis*, D.G. Truhlar, K. Morokuma (Eds)., ACS Symposium Series vol. 215, American Chemical Society, Washington, 1999.
[4] Koch W., Holthausen M. C., *A Chemist's Guide to Density Functional Theory*, Wiley-VCH, New York, 2000.
[5] Gross A., *Theoretical Surface Science. A Microscopic Perspective*, Springer, Berlin, 2003.
[6] Efremenko I., J. Molecular Catal. A, 173 (2001), 19.
[7] Paul J.-F., Sautet P., Phys. Rev. B, 53 (1996), 8015.
[8] Løvvik O. M., Olsen R.A., Phys. Rev. B, 58 (1998), 10890.
[9] Dong W., Hafner J., Phys. Rev. B, 56 (1997), 15396.
[10] Ledentu V., Dong W., Sautet P., Surface Sci., 413 (1998), 518.
[11] Dong W., Kresse G., Hafner J., J. Mol. Catalysis A, 119 (1997), 69.
[12] Okuyama H., Siga W., Takagi N., Nishijima M., Aruga T., Surface Sci., 401 (1998), 344.
[13] Hass G., Menck A., Brune H., Barth J. V., Venables J.A., Kern K., Phys. Rev. B., 61 (2000), 11105.
[14] Lopez N., Illas F., Rosch N., Pacchioni G., J. Chem. Phys., 110 (1999), 4873.
[15] Musolino V., Selloni A., Car R., J. Chem. Phys., 108 (1998), 5044.
[16] Pacchioni G., Rosch N., J. Chem. Phys., 104 (1996), 7329.
[17] Giordano L., Goniakowski J., Pacchioni G., Phys. Rev. B, 64 (2001), 075417.
[18] Vervisch W., Mottet C., Goniakowski J., Phys. Rev. B, 65 (2002), 245411.
[19] Ricci D., Pacchioni G., Sushko P. V., Shluger A., J. Chem. Phys., 117 (2002), 2844.
[20] Neyman K. M., Rosch N., Pacchioni G., Appl. Catal. A., 191 (2000), 3.

[21] *Gaussian 98 (Revision A.9)*, Gaussian Inc., Pittsburgh PA, 1998.
[22] DUNNING T.H., HAY P.J., [in:] *Modern Theoretical Chemistry*; H.F. Schaeffer III (Ed.), Plenum, New York, 1976, p. 1.
[23] HAY P.J., WADT W.R., J. Chem. Phys., 82 (1985), 270; 284; 299.
[24] *Hydrogen in Metals*, Vol. I, II, G. Alefeld, J. Volkl (Eds.), Springer, Berlin, 1978.
[25] BARTCZAK W. M., STAWOWSKA J., Struct. Chem., 15 (2004), 451.

Received 30 May 2005
Revised 28 December 2005