

Hydrogen and oxygen atoms at the metal-support boundary: Pd/MgO and Ni/MgO. A DFT study of the “spillover” effect

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The present work is devoted to computer modelling of interactions and possible migration of atomic: H and O species from the metal surface (Pd, Ni) onto the MgO support surface (the “spillover effect”). The quantum calculations of the present work have been performed using the DFT method (Gaussian code). The hybrid, gradient-corrected functionals for the exchange and correlation and the LANL2DZ basis set have been used in our calculations.

In our analysis the method of the Potential Energy Surfaces (PES) has been applied. The calculations of the H binding energy have been performed for a large number of physically different positions (X,Y) of the H atom over the MgO square with the metal (Pd, Ni) atom adsorbed over the central O ion. Thus we obtain the map of the H atom binding energy as a function of its (X,Y) position. Similar calculations have been performed for O atoms adsorbed on the Ni/MgO and on the Pd/MgO clusters.

The binding energy of the H atom on top of Ni atom is -3.18 eV. Along the O-O axis the H binding energy increases up to -2.25 eV and then decreases again down to -3.20 eV at the O site. One can conclude that the transfer of the H atom from the Ni to MgO surface is an energetically neutral (reversible) activated process (1 eV) and both the direct and the reverse spillover of hydrogen are thus possible. Similar results were obtained for the H atom interacting with the Pd(MgO) system. 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 about 0.5 eV and the activation barrier of about 0.4 eV.

The position of O atom at the top of Pd or Ni atom is unstable. The transfer of the O atom from the position on top of the metal atom to the energy minimum near the Mg site results in about 0.9 eV of excess energy.

The results suggest the possibility of relatively easy transfer of the adsorbed species from the metal to metal-MgO boundary. This is essential for the possibility of the surface reactions: the phase boundary around the metal island collects the adsorbed atoms which spillover from the metal catalyst and makes the stage for numerous surface reactions.

1. INTRODUCTION

An important model of catalysis is represented by the behaviour of the simplest molecule, H_2 , dissociating at the surfaces of the 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].

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

Recent years brought a continuous stream of papers which were devoted to the problem of hydrogen adsorption on metals, in particular on palladium. Full citation of all the papers needs probably a separate review. Numerous references are also given in the recent book by Gross [2] which includes a detailed treatment of hydrogen interaction with Pd. A number of authors applied the DFT method with local density approximation and generalized gradient approximation (GGA) as well as with periodic boundary conditions. For instance Paul and Sautet [3] and Løvvik and Olsen [4] investigated the adsorption of atomic hydrogen on a palladium [111] surface. GGA calculations are also presented in the papers by: Dong and Hafner [5], Ledentu *et al.* [6] and Dong *et al.* [7]. Okuyama and co-workers [8] 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 also a subject of numerous theoretical and experimental papers [9, 10, 11, 12, 13, 14, 15]. The 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. The oxygen sites of the MgO lattice make the preferred metal positions. The calculations reported in [16] of the interaction of a single Pd with MgO predict the binding energy on top of the O site as 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.* [13] performed the calculations of the Pd deposit on the MgO surface. They also

found the favourable adsorption of Pd over the oxygen vacancies. Vervish and co-workers [14] applied the *ab initio* quantum chemical calculations and the second moment approximation to the analysis of the development of the structure of larger Pd clusters on the MgO surface.

In contrast with numerous studies of the metal adsorption on the MgO surface, we do not know about 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 the interactions of the atomic hydrogen or oxygen with the surface of MgO and particularly the H or O interactions with the MgO surface containing adsorbed Pd or Ni atoms and investigate the possibility of the transfer of the H or O atoms from metal onto the MgO surface.

2. METHODOLOGY OF THE CALCULATIONS

The quantum-chemical calculations were performed using the DFT part of the Gaussian 98 [17] suite of programs. The gradient-corrected Becke functional for the exchange has been applied in our calculations. We used the Perdew – 1986 correlation functional and combined it with the former functional to the form of the B3P86 hybrid functional (the code words B3P86, B3LYP, etc. for different functionals are commonly accepted and explained, for instance, in the Koch and Holthausen book [18] where all the necessary references are given). In order to check the sensitivity of the calculations to the exchange-correlation functional we performed the calculations of the hydrogen binding energy to metals and to MgO for the B3LYP and B3PW91 hybrid functionals and the standard BP86 functional. We found that different functionals give the Potential Energy Surfaces (PES) with almost identical geometry. The energy surfaces are slightly shifted (by about 0.1 eV) for different methods.

For all the calculations reported here the LANL2DZ basis set was used. This is the full double-zeta set [19] which includes the Los Alamos effective core potentials due to Hay and Wadt [20]. The BSSE correction was calculated for the H atom interaction with the Pd₅ 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. The 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 the BSSE is very high, and the BSSE does not change the potential barrier heights for the H atom movement, we decided to omit it from the calculations of the H atom transfer from metal to MgO which even without BSSE are very time-consuming.

In the calculations concerning the 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. The calculations based on the periodic boundary conditions have strong drawback of replicating also adsorbed atoms and imposing the artificial layer structure on the system, therefore we selected another way of calculations. The bound hydrogen atom carries rather a 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 $6.6 \times 10^{-31} \text{ m}^3$. This allows us to expect rather small influence of the distant ions of the H atom binding energy. To include the effect of the MgO ionic lattice we surrounded the cluster with the point charges. We performed a series of calculations of a large MgO cluster and found the following Mulliken charges on the Mg and O sites: the charges on the O sites were between $-0.91 e$ and $-1.18 e$, on the Mg sites between $0.96 e$ and $1.3 e$; hence we assumed the unit values of the point charges, rather than the nominal $\pm 2e$. The calculations repeated for the increasing number of the point charges show that the system of 12×12 charges in a single layer $\times 4$ layers is large enough to ensure the convergence of the binding energy. It appears that for the hydrogen atom the contribution is negligible, of the order of 0.01 eV . The contribution scales linearly with the assumed site charge and, therefore, it is also negligible for the $\pm 2e$ charges.

We studied the system composed of a hydrogen (oxygen) atom and a small number of metal atoms (from M_1 to M_3) adsorbed at the MgO surface. The calculations have been performed for a large number of physically different positions (X,Y) of the H atom inside the region of the surface MgO cell containing a metal atom. For a given (X,Y) point we performed the calculations of the energy of H-M-(MgO)_n system for different heights Z of the H atom above the MgO surface plane and found the Z_{opt} that gives the lowest energy of the system. The calculations were performed for the lowest possible spin states. After subtraction of the energy of the separated M-(MgO)_n cluster and the H atom we obtain the three-dimensional plot of the H atom binding energy as a function of its (X,Y) position. The plot of $E_b(X,Y,Z_{\text{opt}})$ forms the Potential Energy Surface (PES).

3. RESULTS AND DISCUSSION

3.1. Calculations of the energy surface for H or O atoms interacting with the MgO clusters

Figure 1 shows the energy surface for the H atom interacting with the MgO surface. The cluster of 8 MgO pairs in the single layer with the geometry of the surface of the MgO crystal (fcc [100] structure) has been assumed in the calculations. The cluster was embedded into the system of four layers of point

charges described in the previous chapter, 560 charges altogether. The calculations were performed for 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 different heights Z of the H atom above the MgO plane and found the value of Z_{opt} that produces the lowest energy of the system. The binding energy of H atom has been calculated as the difference of the total energy of the H(MgO)₈ cluster and separately the energy of the H atom and the (MgO)₈ cluster.

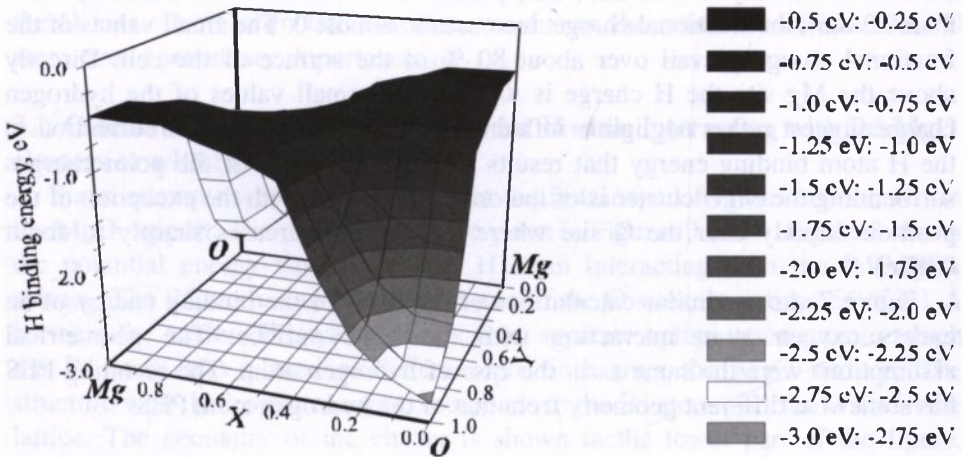


Fig. 1. A 3-D plot of the binding energy surface of an H atom in different positions over the (MgO)₈ cluster surrounded by point charges. For a given position (X,Y) over the MgO cell the distance Z of the H atom from the MgO plane was optimized in order to obtain the highest binding energy. The unit on the X and Y axes is 2.106 Å.

The analysis of the surface shows large differences in energy between different places in the MgO cell. The energetically favourable place for the H atom is over the O²⁻ ion. The binding energy is about -2.79 eV. It is interesting to note that the region of minimum energy is near the oxygen site, the energy over the remaining part of the cell is 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 rather excludes the possibility of easy migration of H atom over the MgO surface. The potential barrier along the oxygen-oxygen line is about 2.11 eV. However, we can not exclude the jumps to the neighbouring oxygen sites either by the over-barrier mode (catalytic processes frequently proceed at rather high temperatures which makes the activated jumps

rather easy) or by the under-barrier (tunnelling) mode even at lower temperatures.

The results of the calculations included also the 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 center 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 at the diagonal line connecting the O sites, roughly halfway between the O site and the cell center.

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 the 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.

Figure 2 shows similar calculations of the PES for the binding energy of an excess oxygen atom interacting with the MgO surface. The geometrical assumptions were the same as in the case of hydrogen atom. The resulting PES has somewhat different geometry from that of the hydrogen atom PES.

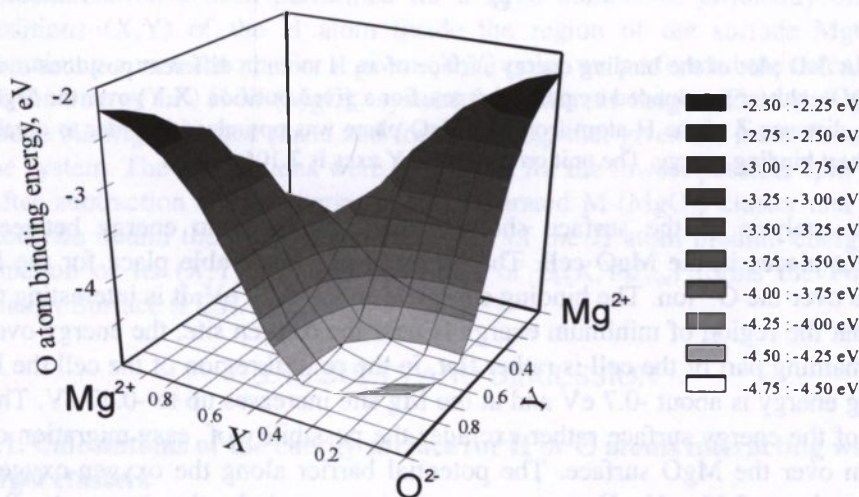


Fig. 2. A 3-D plot of the binding energy surface of an O atom in different positions over the (MgO)₈ cluster surrounded by point charges.

The overall binding energy is much stronger and the favourite binding site of an excess O atom is not exactly at the top of the lattice O ion but is shifted towards the MgO cell centre, halfway between the lattice O site and the cell centre. The binding energy of an excess O atom at the minimum is -4.66 eV (at the distance of 1.32 Å from the surface plane), at the top of the lattice O site is -4.33 eV, at the top of the lattice Mg site is -2.21 eV. The result is unusual at a first sight: an excess O atom is bound more strongly the O lattice site than the Mg site. The explanation comes when we plot the electron density isosurfaces for the system. The Mg ions are deprived of their valence electrons and the electrons of the excess oxygen can form the chemical bonds only with the valence electrons of the O ions. The electrostatic interactions, due to the neutrality of an excess O atom, are of secondary importance.

3.2. Calculations of the energy surface for H atom interacting with Pd-MgO clusters or with Ni-MgO clusters

Some attempts were made to explain the H transport from metal (Pd, Ni) to the MgO support. The results for Pd are given in Figures 3 and 4. Figure 3 shows the potential energy surface for the H atom interacting with the Pd(MgO)₆ system. The Pd atom was placed over one of the O sites, at a distance of 2.1 Å between the nuclei. This value results from separate optimization 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 to the previous calculations of H-MgO the cluster was surrounded by the system of the point charges.

The upper figure shows the energy surface. It appears that the hydrogen binding energy has a local minimum of -2.5 eV for the position of H atom directly above the adsorbed Pd atom. The minimum is surrounded by a flat, roughly circular region with the radius about 1 Å and with the 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 plot of the binding energy along the O-O axis is shown in Figure 4. After crossing the second barrier, there is observed 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 about 0.4 eV.

Figure 4 gives more information about the H atom transfer. The lower part of the figure shows the H binding energy 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 the isosurfaces of the electron density for $\rho=0.08 \text{ e}/\text{\AA}^2$ as the gray shaded regions. The small spheres indicate the positions of 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 a 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 it is not completely broken.

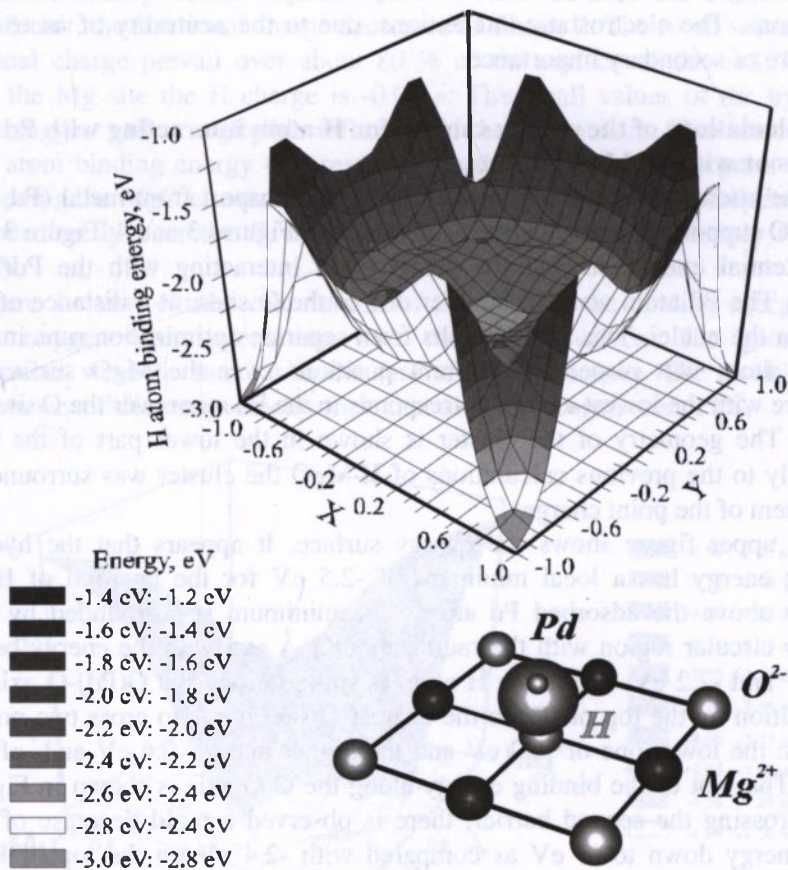


Fig. 3. The binding energy surface for the H atom in different positions over the MgO cell with the adsorbed Pd atom. The Pd atom is placed over one of the oxygen sites in the MgO lattice at the height of 2.1 Å. The H-Pd(MgO)₆ cluster is surrounded by the system of 12 × 12 × 4 point charges. The unit on the X and Y axes is 2.106 Å. The geometry of the system is shown in the lower part of the figure.

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 has not been formed yet due to a large distance between the reacting centers. 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 the prior breaking of the H-Pd bond without the possibility of energy compensation from the newly formed H-O bond. The H atom transfer results in the translation by about 4.1 Å: 2.97 Å in the horizontal and 2.8 Å in the vertical directions. The distance is very large on the scale of the chemical bonds. Thus, the transition state may be interpreted as the one in which the H-Pd bond is already broken and the H-O bond is only beginning to form.

H-Pd/MgO system

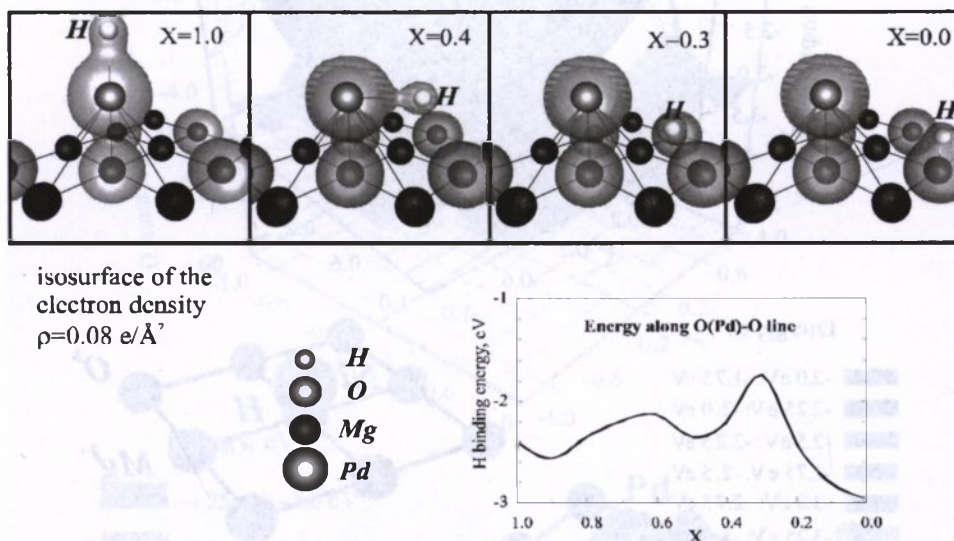


Fig. 4. (Upper part) Isosurfaces of the electron density ($\rho=0.08 \text{ e}/\text{\AA}^3$) for the H-Pd(MgO)₆ cluster with H atom in different positions along the O(Pd)-O diagonal. The positions of the Mg, O and Pd, H atoms are marked as small grey spheres. (Lower part) The H atom binding energy to the Pd(MgO)₆ cluster along the diagonal in the MgO cell.

Summarizing, the 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 is also observed in the experiments – the hydrogen atom comes back to the metal island. The existence of the potential barriers for the spillover transition makes the phenomenon sensitive to the temperature.

Figure 5 shows the results of the calculations performed for hydrogen atom interacting with the MgO surface with Ni atom adsorbed at the top of the O site in the lattice. PES shows the general similarity to the H-Pd/MgO case described in the earlier part. The binding energy of the H atom on top of Ni atom is -3.18 eV.

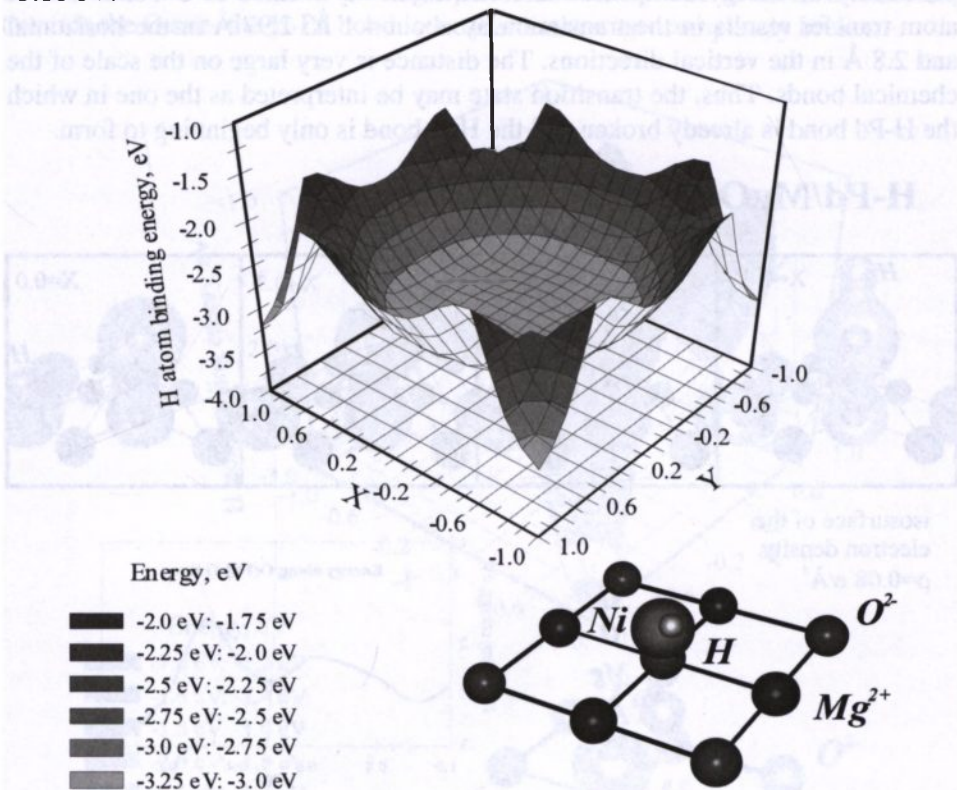


Fig. 5. The binding energy surface for the H atom in different positions over the MgO cell with the adsorbed Ni atom. The Ni atom is placed over one of the oxygen sites in the MgO lattice at the height of 1.86 Å. The H-Ni(MgO)₆ cluster is surrounded by the system of 12 x 12 x 4 point charges. The unit on the X and Y axes is 2.106 Å. The geometry of the system is shown in the lower part of the figure.

Along the O-O axis the H binding energy increases up to -2.25 eV and then decreases again down to -3.20 eV at the O site. The barrier height for the H atom transfer from Ni atom to the O site of MgO is thus about 1 eV and the energy on

the both sides of the barrier is roughly similar. One can conclude that the transfer of the H atom from Ni to the MgO surface is an energetically neutral (reversible) activated process and both the direct and the reverse spillovers of hydrogen are thus possible.

3.3. Calculations of the energy surface for O atom interacting with the Pd-MgO clusters or with the Ni-MgO clusters

Geometry of the potential energy surface for the interaction between an excess O atom with the MgO cluster with Pd atom adsorbed at the top of the O site differs quite significantly from the case of the H atom (Figure 6).

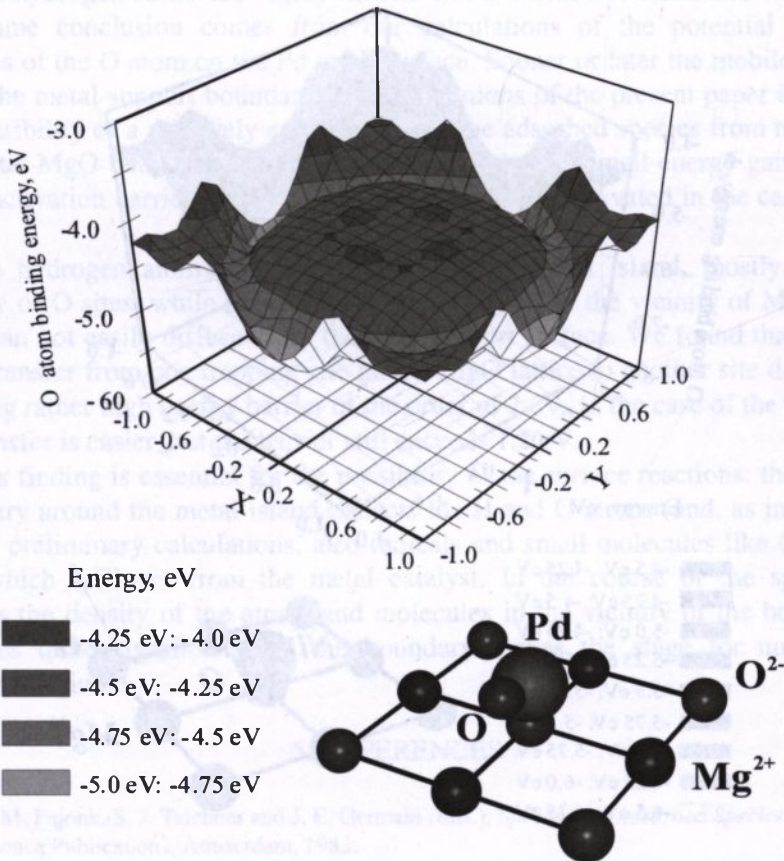


Fig. 6. The binding energy surface for the O atom in different positions over the MgO cell with the adsorbed Pd atom. The Pd atom is placed over one of the oxygen sites in the MgO lattice at the height of 2.1 Å. The O-Pd(MgO)₆ cluster is surrounded by the system of 12 × 12 × 4 point charges. The unit on the X and Y axes is 2.106 Å. The geometry of the system is shown in the lower part of the figure.

First of all, the position of the O atom above the Pd atom is not stable: the centre of the energy surface is occupied by a large flat maximum of a roughly circular shape with the radius of 1.2 Å, with the O atom binding energy about -4.25 eV. When we move away from the central Pd atom the energy decreases, slowly in the immediate vicinity of Pd and then more steeply. The minima at the energy surface, which mark stable positions of the O atom, appear along the Pd/O-Mg line, at a distance 0.2 Å from Mg ions. The minimum energy is -5.11 eV, further along the line the energy increases sharply. The O atom transfer from the position at the top of Pd atom to the stable pockets in the vicinity of Mg ions is unactivated and proceeds with the energy gain of 0.86 eV.

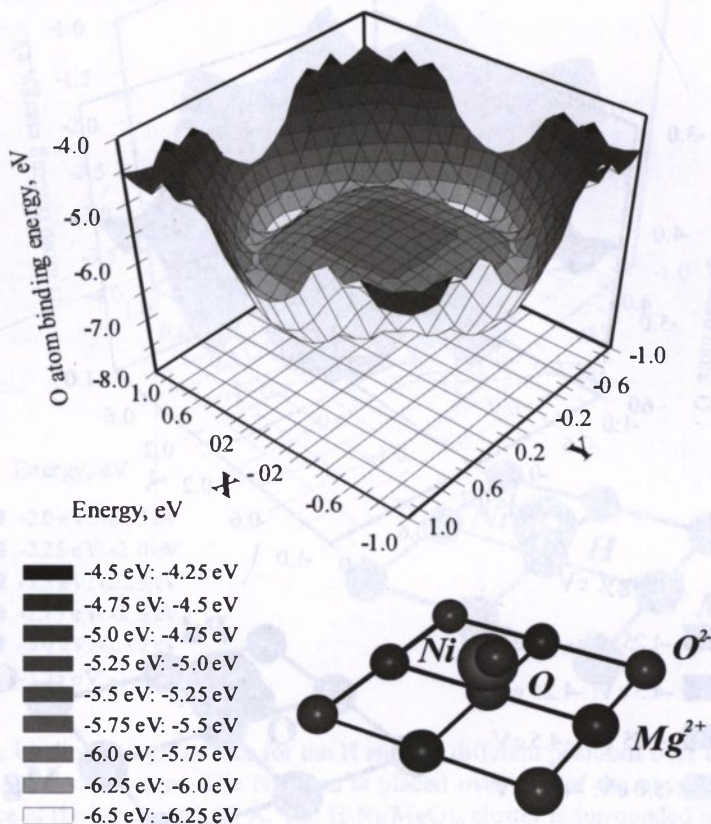


Fig. 7. The binding energy surface for the O atom in different positions over the MgO cell with the adsorbed Ni atom. The Ni atom is placed over one of the oxygen sites in the MgO lattice at the height of 1.86 Å. The O-Ni(MgO)₆ cluster is surrounded by the system of 12 x 12 x 4 point charges. The geometry of the system is shown in the lower part of the figure.

The last figure of the series (Figure 7) shows the PES for the interaction between an excess O atom with the MgO cluster with Ni atom adsorbed at the top of the O site. The potential energy surface is very similar to the Pd case described in this chapter. The binding energy of the oxygen atom is about -5.64 eV at the top of the Ni atom and decreases to -6.54 eV in the vicinity of the Mg site, the energy gain resulting from such a transfer is about 0.9 eV.

4. CONCLUSIONS

Our earlier calculations [21] and reports by numerous authors [22] indicate that the hydrogen atoms are highly mobile on the surface of metal like Pd or Ni. The same conclusion comes from our calculations of the potential energy surfaces of the O atom on the Pd or Ni surface. Sooner or later the mobile atoms reach the metal-support boundary. The calculations of the present paper indicate the possibility of a relatively easy transfer of the adsorbed species from metal to the metal-MgO boundary. The transfer proceeds with a small energy gain and a small activation barrier in the case of H atoms, it is unactivated in the case of O atoms.

The hydrogen atoms are trapped around the metal island, mostly in the vicinity of O sites, while the excess O atoms mostly in the vicinity of Mg sites. They can not easily diffuse away over the support surface. We found that the H atom transfer from one trapping site on the MgO lattice to another site demands crossing rather high energy barrier of the order of 2 eV. In the case of the O atom the transfer is easier, but the barrier still exceeds 1.2 eV.

This finding is essential for the possibility of the surface reactions: the phase boundary around the metal island collects the H and O atoms (and, as indicated by our preliminary calculations, also radicals and small molecules like OH and CO) which spillover from the metal catalyst. In the course of the spillover process the density of the atoms and molecules in the vicinity of the boundary becomes quite significant and the boundary makes the stage for numerous surface reactions.

5. REFERENCES

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