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Density Functional Theory Calculations of Adsorption of Hydrogen on the (100) Titanium Hydride Surface

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Electronic structure calculations based on the density functional theory (DFT) have been applied to the adsorption of hydrogen on the (100) plane of TiH_2. Calculations are performed for a single hydrogen atom placed over a supercell of TiH_2 and the periodic boundary conditions are used, so effectively such system describes a submonolayer coverage. The total energy have been calculated for three different positions of hydrogen over the TiH_2 supercell. The results based on the local density approximation (LDA) and the generalized gradient approximation (GGA) are compared.

Key words: *ab initio* quantum chemical methods, adsorption, density functional calculations, low index single crystal surfaces

The methods based on the density functional theory (DFT) are important tools for the quantum-mechanical calculations of medium scale structures, composed of hundred of atoms. The recent studies demonstrated the usefulness of DFT techniques for predicting such properties of the bulk materials like the total energy, structure and the interatomic distances [1], interaction energy [2], and the density of electron states [3]. The DFT methods may be also applied to more chemically oriented problems like finding the preferred position of an adsorbed atom or molecule on the given surface as they allow one to calculate the binding energy. Many such applications can be found [4–7].

However, the DFT methods are not as straightforward as the direct solution of the Schrödinger equation for the corresponding system. The exact functional for the exchange/correlation contribution is unknown, and there are many different approximations used to describe them. The most popular are the local density approximation (LDA) and the generalized gradient approximation (GGA). The discussion on the validity of these approximations still continues [8–11].

In a common opinion the local density approximation can be successfully applied for predicting the physical properties of a bulk material. In such cases no significant improvement of the results comes from the gradient corrections [12]. For DFT calculations of molecules adsorbed on surfaces the LDA and the GGA are not equivalent. The comparison with experiments suggests that LDA overestimates chemisorption energies on high coordinated sites in a more significant way than the energies of chemisorption on lower coordinated sites. The results obtained for a cobalt atom on Pd (110) surface indicate that GGA gives the energies, which are close to the experimental results [11]. Therefore, one may expect that in the case of surface phenomena the gradient corrections to the energy functional should be taken into account.

Here we would like to discuss a simple system composed of a hydrogen atom on the (100) titanium hydride surface. We consider three possible adsorption sites for the hydrogen atom: on top of Ti atom, over the bridge and in hollow positions coordinated by 3 Ti atoms. We calculate the binding energy of all these sites using both LDA and GGA methods. According to both methods, the bridge positions of hydrogen are the most stable on such surface. Therefore, the most tightly bound hydrogen on the surface occupies similar sites as in the bulk TiH_2.

CALCULATIONS

In this work the MSI Simulation program Dmol^3 has been applied for the variational solution of Kohn-Sham equations of the density functional theory. The density is expressed in the basis of electron densities of atomic orbitals and the program performs all-electron calculation. The spin-restriction calculation, together with an optimized charge density mixing is used to calculate the electronic ground state of a TiH_2 cluster with a hydrogen atom on it. Within the LDA approach we consider exchange-correlation functional of Padrew and Wang (pwc) [13]. Our generalized gradient approximation is based on the Becke, Lee, Yang and Parr (BLYP) exchange-correlation function [14]. The default values of most of Dmol^3 parameters have been used. In order to speed up computations we fixed the SCF density convergence parameter at the level 0.0025. The finite-temperature Fermi function ($T_F = 0.02$) has been used to improve the SCF convergence.

In the calculations we have considered the supercell, which is shown in Figure 1. The (100) surface of Ti atoms is represented by a layer of 5 titanium atoms: one in the center and four at the corners of the cell. The distances between them correspond to the distances on (100) plane of TiH_2 crystal [16]. Below the surface there are 5 additional layers; three of them are composed of 4 hydrogen atoms, and two contain 5 titanium atoms and all the atoms are positioned as in the TiH_2 crystal. The distance between the upper layer of titanium and the lower layer of hydrogen is 5.3482 Å. We use the periodic boundary conditions to expand the supercell in space. Therefore, the titanium atoms at the corners and at the faces belong also to the neighboring cells. The supercell contains effectively 6 titanium atoms and 12 atoms of hydrogen, thus its stoichiometry is the same as in the TiH_2 crystal. We have not optimized the surface structure of TiH_2,

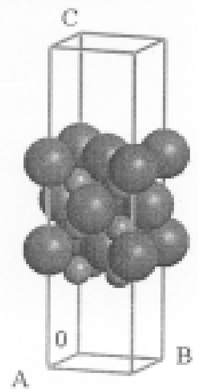

Figure 1. The view of supercell representing TiH_2. The titanium and hydrogen atoms are represented by large and small spheres respectively. The distances are: OA = 4.528 Å, OB = 4.528 Å, OC = 27.5 Å [16]. The ratio of hydrogen and titanium atoms in this supercell is 2:1.

because for a small number of atoms in our calculations, it may lead to artificial results. In the following we consider a hydrogen atom placed on the upper layer of Ti. Because of the periodic boundary conditions, a single atom over a supercell represents a submonolayer coverage of the surface. We think that the distance OC = 27.5 Å is large enough to neglect the interaction between the hydrogen atom placed on the top layer of titanium atoms with the image of the lower layers of titanium and hydrogen.

We have considered three types of hydrogen adsorption sites at the surface: at the top of the mid titanium atom, at the center of the bridge linking the central atom with one of the corner's ones and finally over the center of the triangle formed by the central Ti and two neighboring corner ones. This last position of the hydrogen atom will be called the hollow site. The pictorial representations of these positions are shown in Figure 2. Due to the periodicity of the system, a single hydrogen atom over a supercell means that, depending on its position, 50% of all top sites or 25% of bridge and hollow sites are occupied. In the simulations we calculated the total energies of the TiH_2 supercell with the adsorbed hydrogen atom for a number of different distances between the atom and the surface. The results obtained within LDA and GGA are presented in Figures 3, 4 and 5. In order to see more clearly the energy of interaction between hydrogen and the surface, we have extracted the energy of a system composed of the supercell and a hydrogen atom at a large distance from it from the total energy of the supercell with a hydrogen on its surface. The calculations have shown, that when the distance between a hydrogen atom and the surface exceeds 6 Å, then the total energy hardly depends on this distance and on the position of hydrogen. The interaction energies, given in the paper, represent the adsorption energy per one hydrogen atom in a submonolayer coverage rather than a binding energy for a single hydrogen atom. The interaction energy may be slightly smaller than the binding energy, because of the repulsion between hydrogen atoms in a submonolayer, however, due to a large distance between hydrogen atoms (4.528 Å), we believe that it is a good approximation of the binding energy. To get a better approximation one needs to perform calculations for larger supercells, which is beyond our reach.

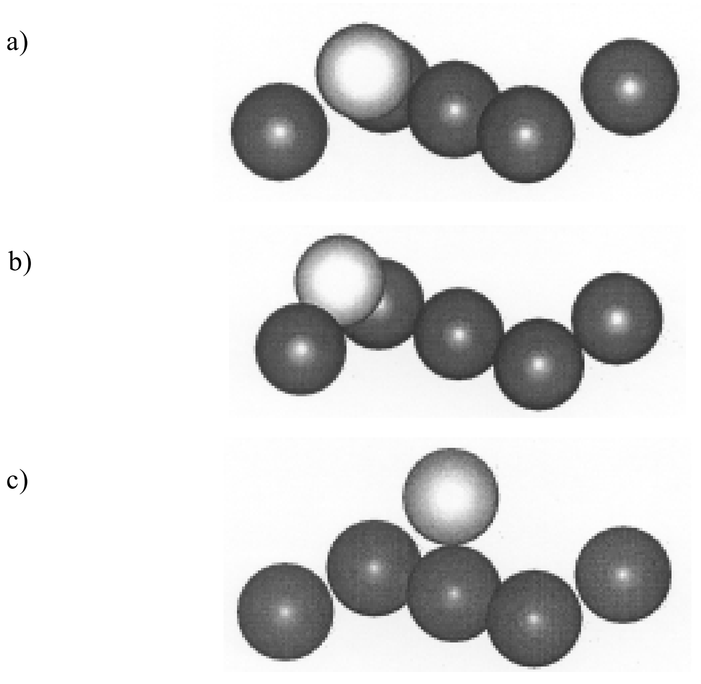

Figure 2. The ball representation of the different adsorption sites of hydrogen atom on TiH_2 surface; (a) – the bridge position, (b) – the hole position, (c) – the top position. The total energy is calculated as a function of the distance between the hydrogen atom and the plane of titanium atoms.

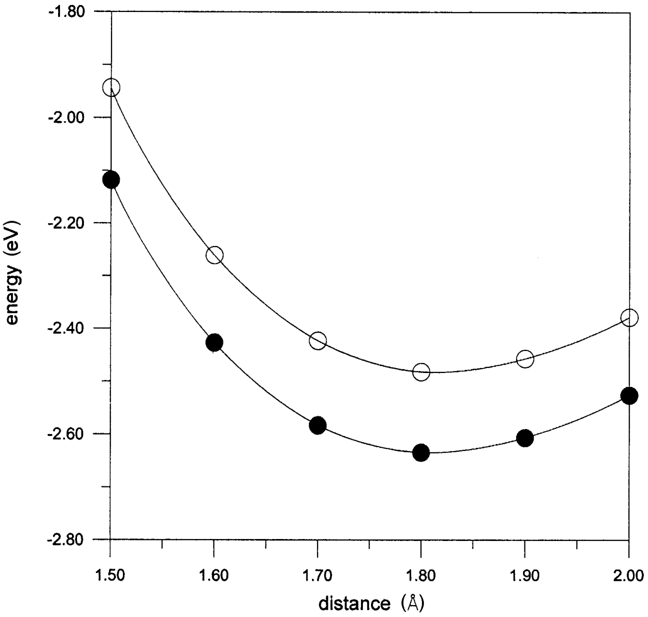

Figure 3. The interaction energy of a hydrogen atom in the top position over TiH_2 (100) surface as a function of the distance from the surface. Results of LDA are represented by black dots, those of GGA by open symbols.

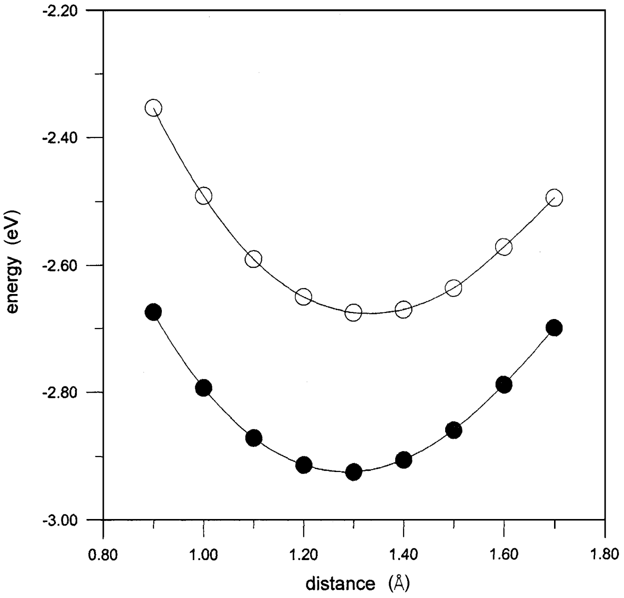

Figure 4. Same as Figure 3 for a hydrogen atom in the bridge position.

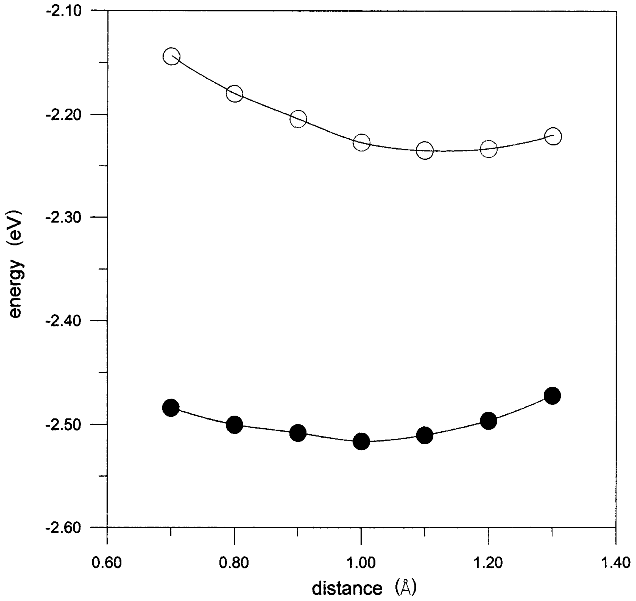

Figure 5. Same as Figure 3 for a hydrogen atom in the hollow position.

RESULTS AND DISCUSSION

Figure 3 shows the energy of interaction for a hydrogen atom in the top position as a function of the distance from the surface. The results for the LDA (dark dots) are compared with these for the GGA (open dots). In both cases the most stable position of the hydrogen atom is around 1.81 Å above the surface. As observed in other studies on the binding energy, the values obtained from LDA is bigger than this coming from GGA, but the difference is not large (here around 10%).

The energies of interaction for a hydrogen atom over the bridge and the hollow positions are shown in Figures 4 and 5 respectively. The adsorption energies (*i.e.* the maximum of interaction energy) for a hydrogen atom placed over three considered sites on TiH_2 (100) surface are given in Table 1.

Table 1. The adsorption energies and the most stable distances for one hydrogen atom on TiH_2 surface. The results calculated by the LDA and GGA methods are compared.

	Top site		Bridge site		Hole site	
	d [Å]	E_0 [eV]	d [Å]	E_0 [eV]	d [Å]	E_0 [eV]
LDA	1.809	2.63	1.283	2.92	1.005	2.51
GGA	1.816	2.48	1.329	2.68	1.139	2.24

It comes out that the adsorption energy at the bridge site is the largest one, so these sites should be occupied first. Therefore, the most tightly bound hydrogen atoms over TiH_2 surface occupy similar sites as the hydrogen atoms in a crystal, but the distances are different. In a crystal the distance between the layers of hydrogen and titanium is 1.070 Å, whereas for the hydrogen atoms on the surface is 1.329 Å above the titanium layer.

The adsorption energies as well as the distances predicted by LDA and GGA methods agree. The energies coming from LDA are by about 10% larger than those obtained using GGA, and both methods indicate that the bridge site is the most favoured on the free surface.

The adsorption energies at all three sites considered are much higher than the adsorption energy observed in experiments [15]. Therefore, we think that hydrogen atoms at these sites remain at the surface of TiH_2 crystal during the experiments. High values of the binding energies at all considered sites suggest that the surface of TiH_2 is covered by a few layers of strongly adsorbed hydrogen and a weakly adsorbed hydrogen, which may be thermally desorbed and which appears at the top of them. The calculations, which should bring information on weakly adsorbed hydrogen on TiH_2, are in progress.

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