

On Hydrogen Layers 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 TiH₂. Calculations have been performed for a supercell of TiH₂ and the periodic boundary conditions have been used. Three different monolayers, two double layers and one selected submonolayer of hydrogen have been considered. It is shown that the most dense coverage corresponds to a submonolayer composed of atoms in the bridge position with respect to titanium atoms on the surface. Both, binding energy and the hydrogen density on the surface agree with the experimental results.

Key words: *ab initio* quantum chemical methods, adsorption, density functional calculations, hydrogen, titanium hydride

The methods based on the density functional theory (DFT) have become basic tools for quantum-mechanical calculations of medium scale structures, composed of hundreds of atoms. The DFT techniques may be applied 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 are also useful for chemically oriented problems, like finding the preferred position of an adsorbed atom or a molecule on a given surface, because they allow to calculate the binding energy [4–8].

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 contributions is unknown, and there are many different approximations used to describe them [8–11]. The simplest is the local density approximation (LDA), which can be successfully applied to predict the physical properties of a bulk material [12]. However, the comparison of DFT calculations for molecules adsorbed on surfaces with experiments indicates, that LDA overestimates the chemisorption energies on high coordinated sites in a more significant way than the energies of chemisorption on lower coordinated sites. Another approximation – the generalized gradient approximation (GGA) – gives binding energies, which are in a better agreement with the experimental data [11]. Therefore, GGA has been used to obtain the results presented below.

In this paper we present calculations of the binding energies for hydrogen layers on the (100) titanium hydride surface. Previously [13], we were concerned with a single hydrogen atom over a TiH_2 supercell. The considered supercell is presented in Figure 1. The (100) surface of TiH_2 crystal 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 [14]. Below this surface there are 5 additional layers; three of them are composed of 4 hydrogen atoms each and two contain 5 titanium atoms. All atoms are positioned as in the TiH_2 crystal [14]. The slab thickness, *i.e.* the distance between the upper layer of titanium and the lower layer of hydrogen, is 5.3482 Å. We have used 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. Thus, the supercell contains effectively 6 titanium atoms and 12 atoms of hydrogen and its stoichiometry is the same as in the TiH_2 crystal. Our calculations have been performed for three adsorption sites, at which the hydrogen atom may be placed: on the top of Ti atom, over the bridge linking the central Ti atom with a corner one and in the mid between two corner Ti atoms. We have found that the bridge site is the most adsorbing one and that the binding energy exceeds 2.5 eV (2.92 eV within LDA and 2.68 eV within GGA). Such strong binding of hydrogen with the surface suggested that a layer or even a few layers of hydrogen atoms may cover the surface of TiH_2 at low temperatures. In the following we show results of calculations for a high coverage and discuss the stability of hydrogen layers considered.

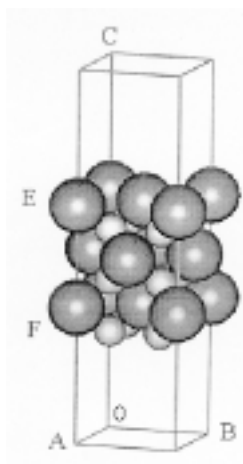


Figure 1. The considered supercell of TiH_2 . The titanium atoms are marked as dark balls and the atoms of hydrogen as the light ones. The distances are $OA = 4.528$ Å, $OB = 4.528$ Å, $OC = 27.5$ Å and $EF = 5.3482$ Å.

CALCULATIONS

The MSI Simulation program Dmol³ [15] has been applied to obtain a 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-compensated calculation, together with the optimized charge density mixing, is used to obtain the electronic ground state of a TiH₂ slab with a number of hydrogen atoms on it. The generalized gradient approximation is based on the Becke, Lee, Yang and Parr (BLYP) exchange-correlation function [16]. The default values of most of Dmol³ parameters have been used. In order to speed up computations, we fixed the SCF density convergence parameter at the level 0.00025. The finite-temperature Fermi function ($T_F = 0.02$) has been used to improve the SCF convergence. We have not optimized the surface structure of TiH₂, because for a small number of atoms considered, it may lead to artificial results. We also think, that the distance OC–EF ≈ 22.1 Å is large enough to neglect the interaction between the hydrogen layers, placed on the top titanium atoms with the image of the lower layers of titanium and hydrogen.

We define the interaction energy between the surface and an adsorbed layer of hydrogen in the following way:

$$E_I(\vec{r}) = \frac{1}{N} (E_{SL}(\vec{r}) - E_S - N \cdot E_H)$$

where E_{SL} is the energy of the slab with a layer of hydrogen at the position r with respect to the slab, E_S is the energy of considered TiH₂ supercell and E_H is the energy of a free hydrogen atom (-13.6 eV). N denotes the number of hydrogen atoms in the layer, so E_I is calculated per a single atom in the layer. E_I shows how the energy of a hydrogen atom in a layer differs from the energy of a separated hydrogen atom.

RESULTS AND DISCUSSION

Let us consider three different monolayers of hydrogen on (100) TiH₂ supercell, located as shown in Figure 2. In these monolayers hydrogen occupies all bridge (Fig. 2A), top (Fig. 2B) or hole positions (Fig. 2C) on the surface. It can be seen that all monolayers, treated as a whole, have a stable position with respect to TiH₂ surface. Table 1 shows the binding energy (*i.e.* the absolute value of the interaction energy at the most stable position of a monolayer) per one atom of hydrogen, calculated with respect to the energy of a hydrogen atom. The distances corresponding to the most stable position are also given. It comes out that the monolayers composed of hydrogens in the bridge and top positions are characterized by the largest binding energies, slightly exceeding 2.1 eV/atom. It is clear that all monolayers considered are more stable than separated hydrogen atoms, but if we compare the binding energies with the binding of hydrogen atom in molecule (2.45 eV) we find that none of them is globally stable, as it should decompose into individual molecules. The value 2.45 eV is the binding energy per hydrogen atom in the ground state of a hydrogen molecule in OA OB OC cell calculated using Dmol3/Cerius2v4.0 program. Of course, there are more precise results (2.373 eV [17,18]), but in this paper we consequently use numbers coming from one DFT GGA method.

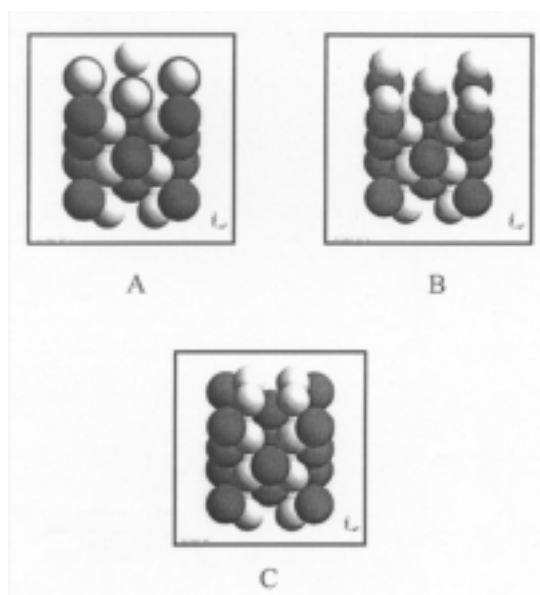


Figure 2. The considered hydrogen monolayers on TiH_2 surface; 2A, 2B and 2C show monolayers of hydrogen at the hollow, the top and the bridge adsorption sites respectively.

Table 1. The binding energy per one atom of hydrogen in monolayers containing hydrogen atoms in top, bridge and hollow sites.

	Top site		Bridge site		Hollow site	
	d [Å]	E_0 [eV]	d [Å]	E_0 [eV]	d [Å]	E_0 [eV]
GGA	1.754	2.116	1.029	2.108	0.606	1.98

We have also investigated two double hydrogen layers covering the (100) surface of TiH_2 . We have considered the double layer composed of hydrogens, occupying all the bridge and hollow sites, because the monolayers composed of hydrogens at these sites are characterized by a closed distance to the surface and, thus, we may expect that their binding to the surface is strong. Alternatively, we have considered a double layer of hydrogen placed in the hollow and the top position, because the monolayer related to the top site is characterized by the highest binding energy. The energy of a double layer, as a function of the distances between the monolayers composing it from TiH_2 surface, is shown in Figure 4 (for the bridge-hollow double layer) and in Figure 5 (for the hollow-top double layer). Our calculations give the distances corresponding to the most stable position of such structure (they can be read from Figures 4 and 5) and the binding energies per a hydrogen atom, which are equal to 1.92 eV (for a bridge-hollow double layer) and 1.91 eV (for a hollow-top one). As expected, the hydrogen in a double layer is characterized by a lower binding energy than for monolayers. Therefore, the double layers are also not stable and they should decompose into hydrogen molecules.

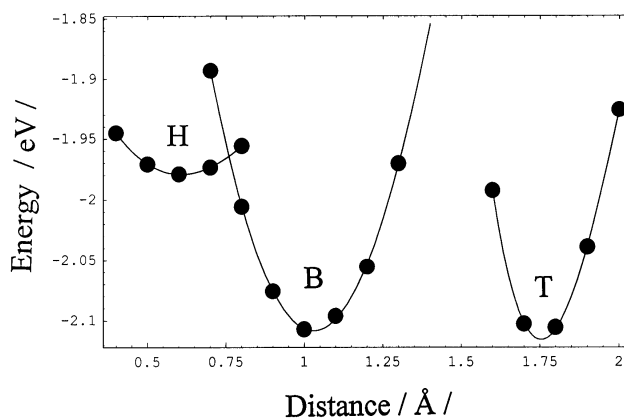


Figure 3. The interaction energy between monolayers and surface as a function of the distance from the surface; T, B, H mark monolayers with H atoms at top, bridge and hollow adsorption sites respectively.

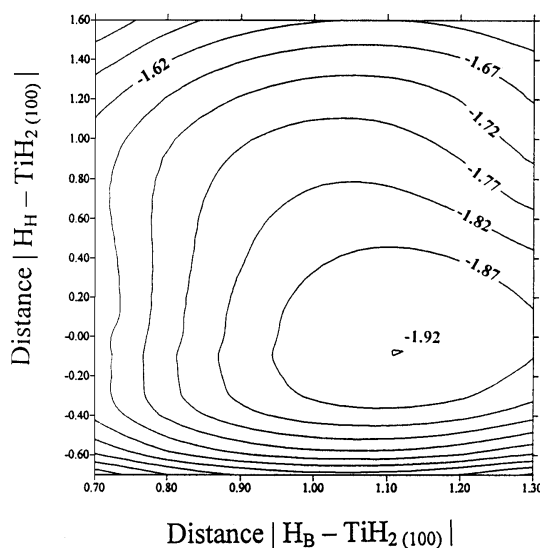


Figure 4. The interaction energy between the double layer composed of hydrogen atoms at bridge and hollow sites, and (100) surface of TiH_2 as a function of the distances of layers from the surface.

Finally, we have considered a submonolayer of hydrogen placing two atoms per supercell at the bridge sites on one of the diagonals. We assumed that both atoms are at the same distance from TiH_2 surface. The interaction energy per atom in such monolayer, as a function of distance, is presented in Figure 6. The results show that the submonolayer formed by hydrogen atoms located in the bridge position is stable and the binding energy is 2.658 eV. The distance between the stable layer and the surface is 1.16 Å, which is slightly shorter than the distance between the surface and a

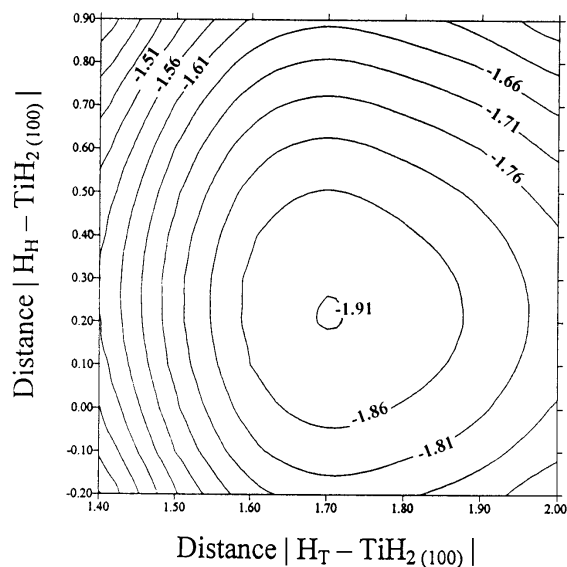


Figure 5. The interaction energy between the double layer of hydrogen atoms at top and hollow sites and (100) surface of TiH_2 as a function of the distances of layers from the surface.

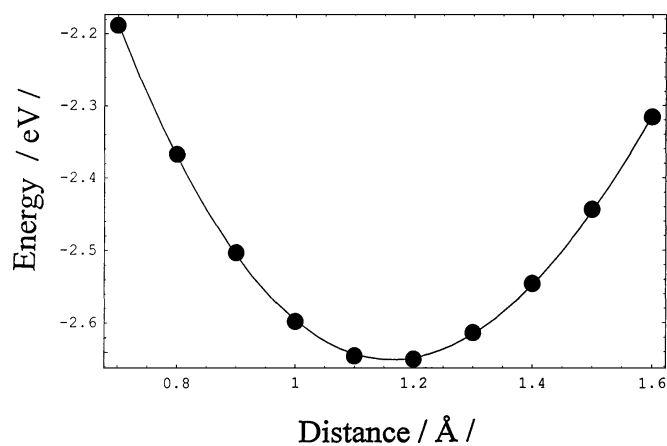


Figure 6. The interaction energy between the 1/2 submonolayer of hydrogen atoms at the bridge sites and the surface as a function of the distance from the surface.

separated hydrogen atom at this position (1.329 Å [13]). We think that the decrease in the distance can be explained by interactions between the “bonding” electron density between hydrogens and the titanium atom below. Such hypothesis is supported by the fact that the monolayer of hydrogens at bridge positions is even closer to the surface – see Figure 3.

CONCLUSIONS

We have applied DFT methods to calculate the stability of monolayers and multilayers of hydrogen on the (100) surface of TiH₂. Despite of the simplifications made (we have not taken into account the reorganization of the topmost levels of TiH₂ and the corrections for the dipole potential [19]) we are able to estimate that the maximum surface density of hydrogen is 9.75×10^{14} at/cm² and that the difference between the energy of absorbed hydrogen atom and the atom of hydrogen in a hydrogen molecule is -0.208 eV. Both, the surface density of hydrogen and the binding energy are in quite a good agreement with experimental results, in which the surface of TiH₂ looked saturated for 5×10^{14} at/cm² and the measured activation energy of hydrogen's adsorption was 0.095 eV per atom [20]. It should be remembered that the experiment was performed not on the (100) surface of TiH₂, but on a random selection of different surface planes.

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