

DFT study of hydrogen adsorption and desorption at Pt edges and terraces for micro- facets of varying sizes

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**Faculty of science
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60 ECTS thesis submitted in partial fulfillment of a
Postgraduate Diploma degree in Chemistry

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Útdráttur

Víxlverkun vetnis við Pt yfirborð af mismunandi gerðum var reiknuð með þéttfellafræði (DFT). Lengd (111) flatanna var aukin frá einni röð Pt atóma til 11 raða til að sjá hvaða áhrif rafeindabygging Pt yfirborðsins hefur á bindingu vetnis við Pt. Með þessu líkani viljum við sjá hvernig vetni binst og myndast á Pt nanó-ögnum (NPs) þegar þær eru stækkaðar. Í öllum tilvikum binst vetnið fyrst við brúnir Pt nanó-agnanna, síðan fyllast flötu yfirborðin, og síðast fyllast Pt atómin sem eru næst við brúnirnar. Við sjáum ótrúlega litla breytingu í rafeindauppbyggingu Pt yfirborðsins og bindingu vetnis við það, þegar yfirborðin eru stækkuð. Losunarorka vetnis frá hryggjunum breytist hins vegar sterklega þegar staðsetningu og fjölda vetnis nágranna á yfirborðinu er breytt, eða frá 0.7 eV þegar engir nágrannar eru til 0.4 eV við hámarksfjölda nágranna.

Abstract

The interaction of hydrogen with edges and terraces of Pt surfaces was studied using density functional theory (DFT) calculations. Length of the (111) micro-facets was varied from 1 to 11 rows of Pt atoms in order to see how the electronic structure of the Pt surface affect the interaction strength between Pt and H. By this modeling, we want to investigate where hydrogen adsorbs and desorbs from Pt nano-particles (NPs) as they become bigger. In all cases, the H starts to cover the edges of the NPs, then the terraces become covered with H, and last the terrace sites next to the edges are filled. We see remarkable small difference in electronic structure and H binding energy as the micro-facets become larger. Desorption energy of H_2 from ridge sites is strongly varying with positions and numbers of the nearest H neighbors on the surface from 0.7 to 0.4 eV.

Table of Contents

Abstract.....	3
Introduction.....	5
Calculation details.....	6
Results	8
Conclusion	14
Reference	15

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Abstract

The interaction of hydrogen with edges and terraces of Pt surfaces was studied using density functional theory (DFT) calculations. Length of the (111) micro-facets was varied from 1 to 11 rows of Pt atoms in order to see how the electronic structure of the Pt surface affect the interaction strength between Pt and H. By this modeling, we want to investigate where hydrogen adsorbs and desorbs from Pt nano-particles (NPs) as they become bigger. In all cases, the H starts to cover the edges of the NPs, then the terraces become covered with H, and last the terrace sites next to the edges are filled. We see remarkable small difference in electronic structure and H binding energy as the micro-facets become larger. Desorption energy of H₂ from ridge sites is strongly varying with positions and numbers of the nearest H neighbors on the surface from 0.7 to 0.4 eV.

Introduction

Platinum is one of the most important metal due to its role in technologie as a catalytic converter and its wide use for jewelry. Catalyst is an important material because of its economic role in the chemical industry for decreasing the activation energy of a specific reaction. What makes Pt a good hydrogenation and hydrogen formation catalyst is its ability to adsorb the protons sufficiently strongly to cover the entire surface, but not so strongly that it is difficult to persuade them to react. Also, the catalyst is very stable under whole variety of conditions, e.g. it does not oxidize or corrote easily. This important role of Pt made us to study the surface of Pt in more detail. The attention was focused on hydrogen adsorption energetics, mobility (diffusion) of adsorbed hydrogen and surface reactivity toward hydrogen formation, i.e. desorption from the surface.

We are concentrating here on the size effect of the surface on the electronic structure of the model and calculating the adsorption energy of H-atom on different sizes of Pt and use that as a measure of the variation of the chemical properties of the surface with different sizes. In other words, we probe the electronic structure with adsorbed hydrogen.

The fcc Pt(110) surface is used as a model in this article by cutting the surface in the direction which gives (111) micro-facets of varying sizes. By this modeling, we mimic a part of Pt nano-particles (NPs) of varying sizes. The surface of Pt(110) has a missing row reconstruction; Pt(110)-(1x2), both the clean surface and the hydrogen covered surface [ⁱ, ⁱⁱ].

In a recent letter by our group [ⁱⁱⁱ], we observed a new mechanism for H₂ formation on the Pt(110)-(1x2) surface. There the ridge sites (similar to edges on a NP) were found to be the active sites of H₂ formation, both at low and high H coverage. At intermediate coverage, the H₂ is formed at the small micro-facet on this surface. Since this micro-facet only consists of one Pt row, it is not clear which sites will be active at intermediate H coverage when the micro-facet becomes larger, as is the case of Pt NPs, which are used for real applications, since they are more active and have larger surface areas. In the present work, we investigated systematically the hydrogen adsorption and formation on model systems having 12 different sizes of the micro-facets. The adsorption energy of H was calculated at the ridge sites and the micro-facets on these different surfaces. The desorption energy of H₂ molecules from ridge sites was calculated as a function of the hydrogen neighbors on the surface.

Calculation details

The density functional theory (DFT) [^{iv}] calculations have been performed for structure relaxation and minimum energy path (MEP) calculations for all surfaces using Vienna ab initio Simulation package (VASP) [^v] with RPBE [^{vi}] functional. All calculations used plane-waves and ultra-soft pseudo potential to represent the ionic cores and 450 eV cutoff for the plane waves was used to describe the valence electrons. Nudged elastic band (NEB) [^{vii}] method was used to calculate MEP for diffusion of atomic hydrogen on Pt surfaces, the activation energy was calculated from the MEP.

The model used for this study is constructed from the Pt(110) surface modeled with 8 and 13 Pt layers. The 8 layered system was used when calculations were only performed for small micro-facets, in particular when only 2 rows of Pt atoms formed the micro-facet (explained below). The 13 layered systems were used in all other calculations, where H-atom attached to the surface was fixed in x and y directions and was allowed to relax in the z direction, where 1D potential energy surfaces (PESs) were constructed. For few test systems we increased the number of layers to 15 and the energetics did not change more than 0.02 eV, indicating we had converged results. Trends in adsorption energies was calculated for Pt surfaces having varying sizes of the micro-facets; from no micro-facets (the unreconstructed Pt(110) surface) to Pt surfaces having 11 Pt rows forming the micro-facet (see Fig. 1). We used 1-2 Pt rows in the direction along the ridge, and 4-24 Pt atoms along the direction of the micro-facets, depending on their sizes. When creating the missing row reconstructed Pt(110)-(1x2) surface we remove every other Pt rows, creating the ridge (R) Pt rows, one facet (F) Pt row, and the trough (T) Pt rows. We name this surface 1-facet in the remaining of the paper. This micro-facet is very small and in this study we want to see the effect in the H adsorption energies when the micro-facet is made larger. We do this in order to investigate how the energetics and the electronic structure changes of the ridge Pt atoms and the micro-facet, when the model becomes more similar to a real NP [viii, ix], which have larger facets as they become bigger. The ridge sites we create by this are having similar structure as the edges of a NP, where two (111) facets meet. We create the 2-facet surface, having 2 Pt rows in the micro-facet, by removing 2 Pt rows in the first layer and one Pt row in the second layer (see Fig. 1). Similar procedure is done in order to create micro-facets having up to 11 Pt rows in the micro-facets (11-facet). Since we are cutting the Pt(110) surface more and more, we need 13 Pt layers in total in order to represent the Pt atoms around the Pt trough sites well enough. It is noted that when having systems with more than 5 Pt rows in the micro-facet (5-facet) we were only interested in the energetics around the ridge. The bottom layers of the slabs were fixed and the two top layers were allowed to relax with the adsorbed hydrogen atoms. The calculations were allowed to converge until the highest force on any movable atom in any direction was not more than 0.01 eV/Å. The slabs were separated by 10 Å vacuum. The calculated lattice constant for Pt was 4.011 Å. A Monkhorst-Pack k-point

sampling was used, where the length (in Å) multiplied with the number of k-points in each direction was never less than 20. Increasing the number of k-points gave us negligible difference.

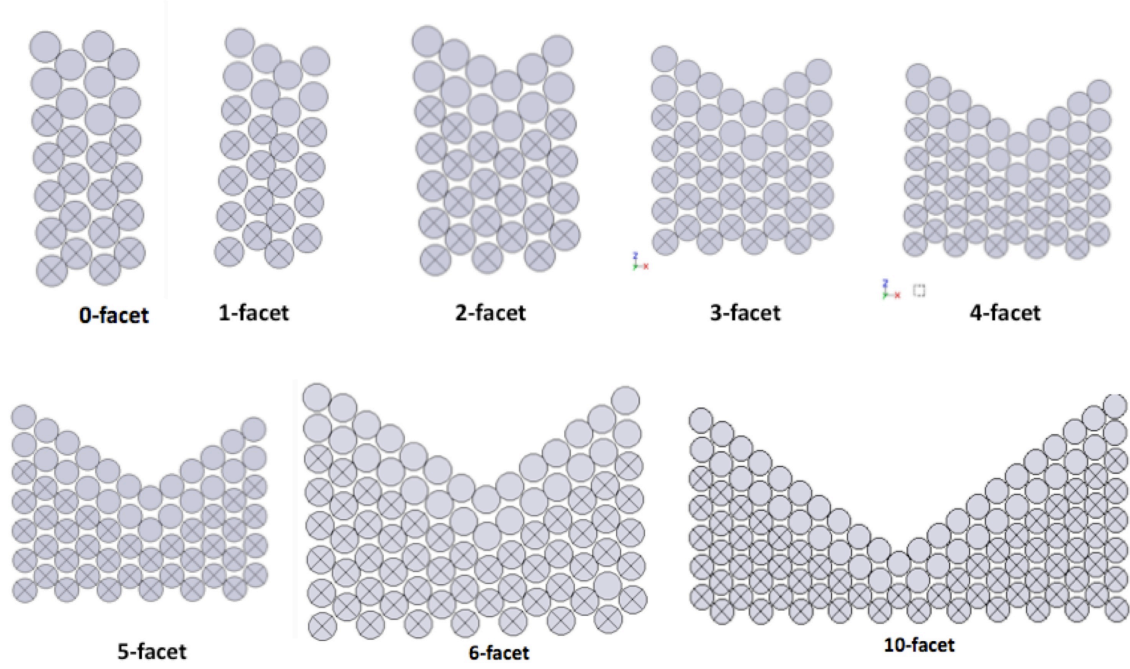


Fig. 1: Side view of few surfaces having varying sizes of the (111) micro-facets.

H-atoms were added to the Pt surfaces at different H coverage and the binding energy of H was calculated from the differential adsorption energy

$$\Delta E_H = E(n) - E(n-1) - 1/2E(H_2)$$

where $E(n)$ is the total energy of the surface with n H atoms adsorbed and $E(H_2)$ is the total energy of isolated H_2 in a box.

Hydrogen coverage was calculated as the ratio of the n number of H-adatoms to the number of Pt atoms on the surface N_{surf}

$$\Theta_H = n/N_{\text{surf}}$$

Results

In order to investigate the preferred order of H adsorption as the H coverage is increased and when the micro-facet gets bigger we start with the 2-facet system. As for the 1-facet system [iii] the strongest binding energy is at the ridge sites (R) initially. After all the R sites have been filled the preferred site is on top of F2 Pt atoms (see Fig. 2a). Adsorbing in T sites or in F1 sites after filling R and F2 has a small energy difference (see Fig. 2b).

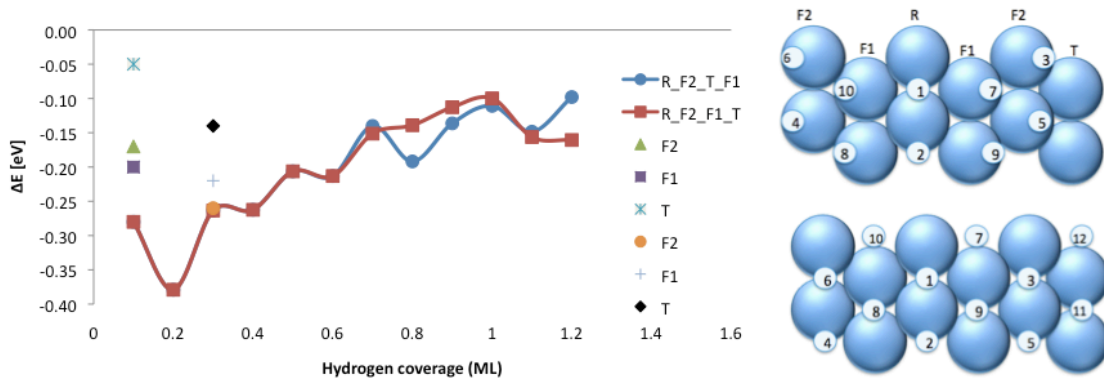


Fig. 2: a) Configuration H adsorbed on the 2-facet Pt surface. R denotes ridge Pt atoms, F1 denotes the first row of Pt atoms on the micro-facet beside the ridge, F2 denotes the second row of Pt atoms on the micro-facet and T denotes trough Pt atoms. b) Differential H adsorption energy as a function of hydrogen coverage. Different order of filling the surface with H atoms was studied: (Blue circles) starting by filling R sites, then F2 sites, then T sites and then F1 sites. (Red squares) starting by filling R sites, then F2 sites, then F1 sites and then T sites. Other possible filling for the initial H atoms is also shown.

Since the F2 sites were preferred over the F1 sites for the 2-facet system, we want to see if that is an artifact from the environment the F2 Pt atoms are located in (the trough atoms are next to the F2 Pt atoms here), or if F2 atoms are perhaps the next strongest adsorption sites in general. Hence, similar calculations were done for the 3-facet Pt surface. The surface was filled with H-atoms in different orders as shown in Fig 3. The strongest H binding energy is forming on R, followed by F2 and then F3 which only has slightly lower binding energy than F2. Finally, F1 and then T sites are filled. If we compare our results with the 2-facet Pt surface (see Fig 2.), we see that the 3-facet surface is filled

with a similar order as the 2-facet surface; R, F2, F3, F1 and T for the 3-facet surface but R, F2, T, and F1 for the 2-facet surface. This indicates that the ridge sites due adsorb strongest as the micro-facets become larger (edges of Pt NPs) but then the micro-facets or the terrace sites become covered with H and finally the Pt atoms next to the ridge sites or edges of the NP get filled.

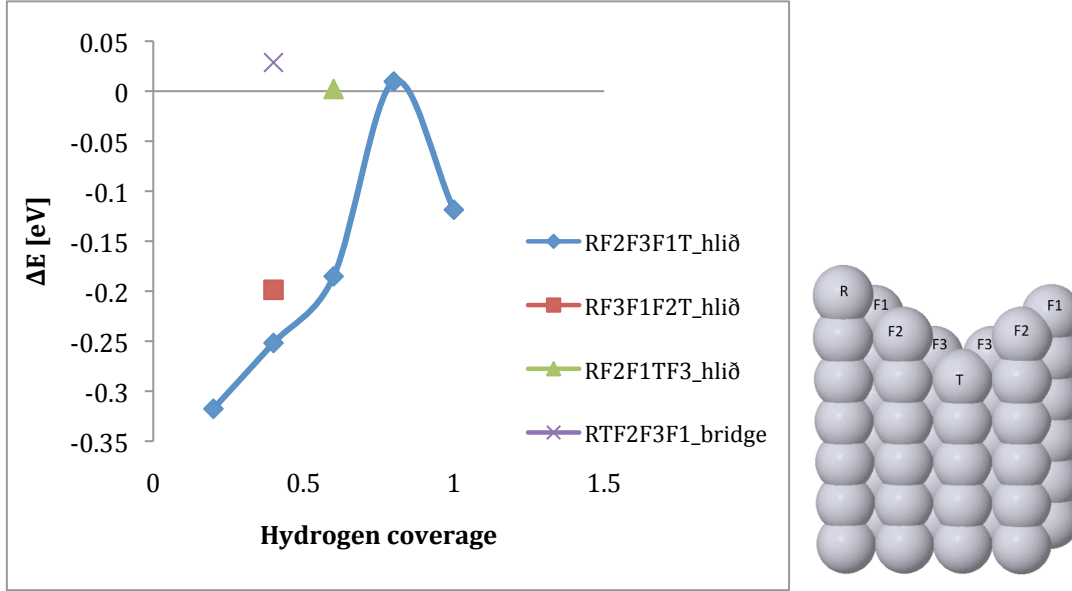
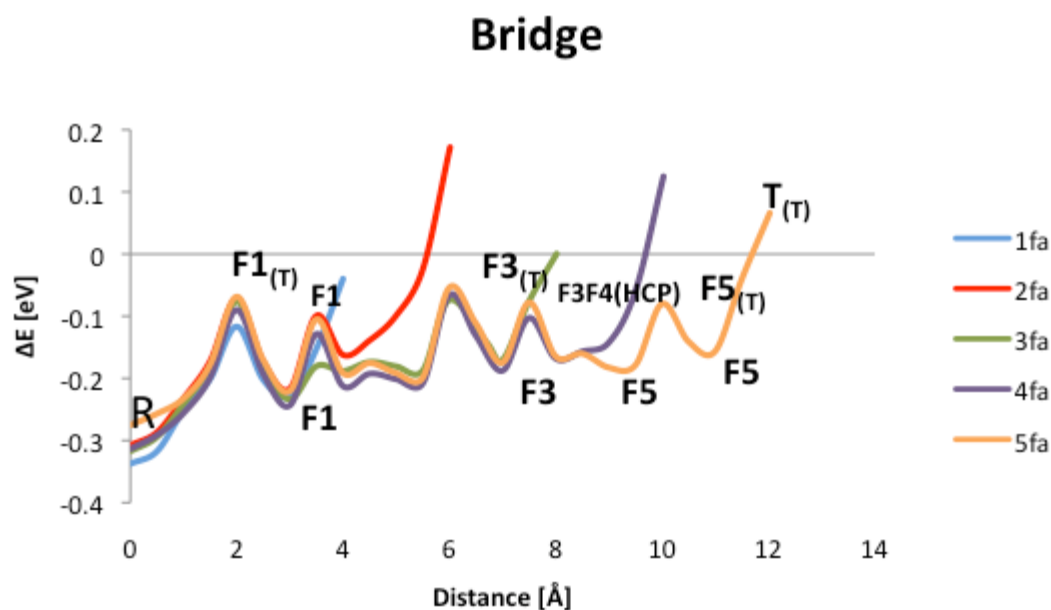


Fig 3: a) Configuration H adsorbed on the 3-facet Pt surface. Same labeling as in Fig 2 for the 2-facet, whereas here the third Pt row has been added to the micro-facet (F3 Pt atoms). b) Differential H adsorption energy as a function of hydrogen coverage. Different order of filling the surface with H atoms was studied: (Blue diamonds) starting by filling R sites, then F2 sites, then F3 sites, then F1 sites and finally the T sites. Other possible binding sites for the H atoms is also shown.

As discussed above for the 2-facet and 3-facet surfaces it seems that the F2 sites are the next sites to be filled after the ridge has been fully decorated. In order to see if or how much the electronic structure is changing as the micro-facets size is increased. We calculate 1D potential energy surfaces (PESs) as the H adatom is translated from the ridge to the trough. We do two different line scans; where the H adatom starts in the energy lowest bridge position on the ridge, and where H starts on-top of a Pt atom at the ridge. The binding energy of H-adatom was calculated on the 5 different surfaces; from 1-facet to 5-facet surfaces (see Fig. 4(a) and 4(b)). We observe remarkable small

difference in the H binding energy (or the electronic structure of the Pt surfaces) as the length of the micro-facet is increased. There is a negligible difference in binding energy strength on all sites except perhaps at the ridge, at the trough, and in a saddle point where the H adatom is between an F1 and F2 Pt atoms, or 3.5 Å away from ridge. Since the trough sites do not exist on NPs, we are only interested in understanding the small difference (around 0.1 eV) at the ridge and at the saddle point 3.5 Å from the ridge.



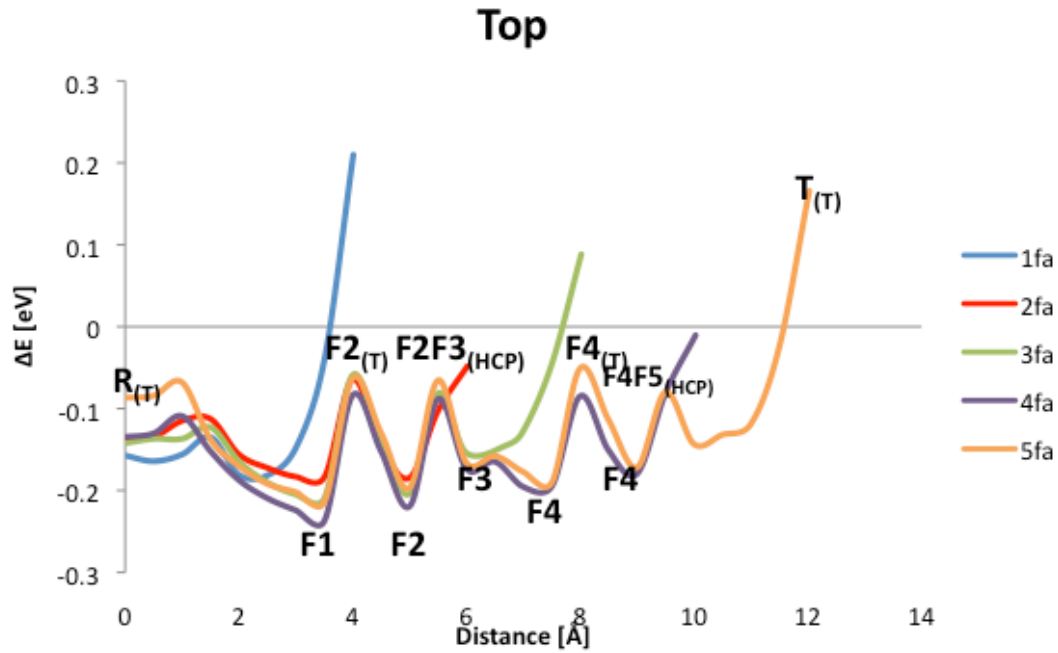


Fig 4: 1D potential energy surfaces (PESs) for H adatom translated from the ridge to the trough on 5 different Pt surfaces; from 1-facet to 5 facet surfaces. In (a) the H adatom starts in a bridge site at the ridge while in (b) the H-adatom starts in an on-top site of a Pt atom on the ridge.

In order to conclude where the small energy difference we observed for the ridge sites and the point 3.5 Å from the ridge is coming from we tested few things. After checking if all parameters were converged such as k-points, number of layers etc, we calculated the H adsorption energy for these two points where the length of the micro-facet was increased even further, to 11-facet Pt surface (see Fig. 5). We also include the none-reconstructed Pt(110) surface for comparison. the length of the micro-facet appears to have very small effect on the electronic structure of the Pt surface and in the H adsorption energy. For the H adsorption on the ridge site in bridge position, the difference between the 1-facet and the 11-facet surface are about 0.1 eV with small variations for the surface sizes in between. When H is in this saddle point position 3.5 Å from the ridge, there is a negligible difference between the 1-facet surface and the 11-facet surface, only 0.02 eV difference. In between, we do have some oscillations, but the fluctuations are only about

0.1 eV in total, indicating that there is in fact always a small difference in the electronic structure, no matter how large the micro-facet is.

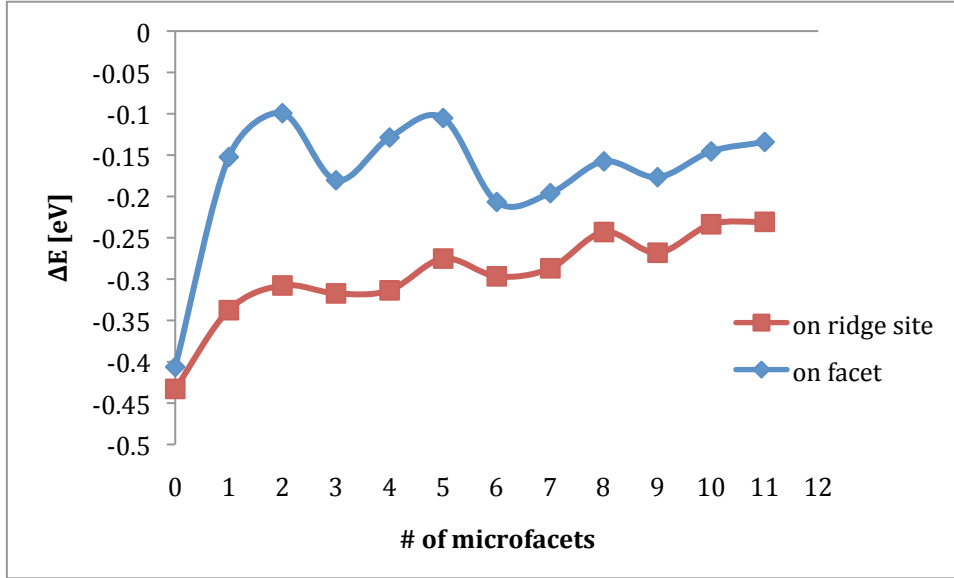


Fig 5. Adsorption energy of H-adatom on 12 Pt surfaces where the smallest one is unreconstructed Pt(110) surface with no micro-facet and the biggest one with 11 Pt rows in the micro-facet. The adsorption energy is calculated in two positions; on bridge at ridge site (red squares), and on the micro-facet 3.5 Å from the ridge (blue diamond). The H adsorption energy is plotted as a function of the number of Pt rows in the micro-facet (# of micro-facets).

Finally, we want to calculate the H₂ desorption energy when H₂ is formed at the ridge of the Pt surface. In our resent paper [iii], we saw that the activation barrier for H₂ desorption from the ridge sites is always less than 0.1 eV higher than the reaction energy or the binding energy of two H adatoms on the ridge. Hence, we can calculate the binding energy of these two H adatoms on the ridge for different H coverage on the micro-facet and in the trough to see the effect of H neighbors on the desorption barrier. In our previous study for the 1-facet surface, we observed large variations in the desorption energy (about 0.3 eV) from the ridge as H adatoms were adsorbed in F', F, and T sites. The strong effects that the F and T sites have are studied further here since the H adatoms in these sites are not as close to the H adatoms at the R sites. We do similar calculations, but now for the 2-facet Pt surface. The desorption barrier from the R sites is decreasing as H-adatoms occupy the F1 Pt atoms on the surfaces shown in Fig 6, or from 0.7 eV with

no H neighbors to 0.4 eV with H neighbors in the F1 sites. The effect of covering the F2 or the T sites with H adatoms (which are now further away from the R sites than on the 1-facet surface) is negligible. However, filling T sites is impacting the F2 Pt atoms by pulling them towards the trough by 0.33 Å and up by 0.24 Å. Similar surface relaxation was also observed for the 1-facet, which was affecting the desorption energy by about 0.3 eV. Since here the micro-facet has been made bigger, the surface relaxation in the F2 Pt atoms do not affect the H₂ desorption energy from the ridge.

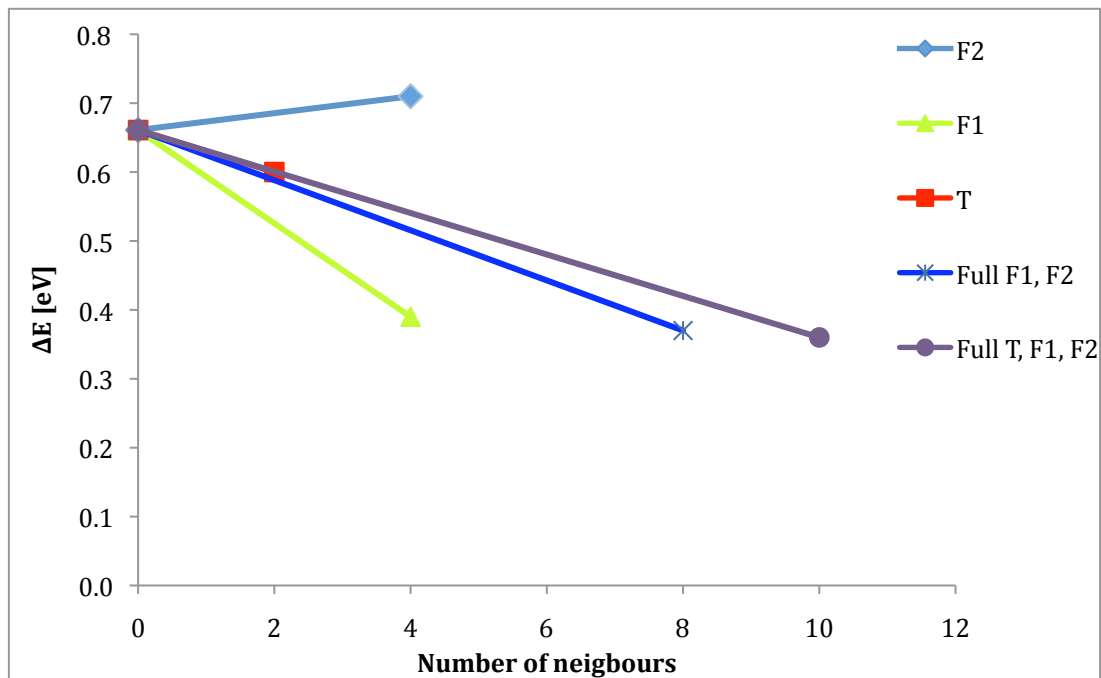


Fig 6: The binding energy of two H-adatoms at bridge on Pt ridge sites, as a function of the number of H adatom neighbors in various types of sites. The binding energy here is similar to the value of the desorption energy as explained in the text.

Conclusions

To summarize the DFT study about hydrogen interaction with various sizes of Pt surfaces our conclusions are:

Increasing the size of the Pt micro-facets is not having a large effect on the adsorption energy of H to the surface, indicating a small change in the electronic structure of the surface. By increasing the length of the micro-facets we have obtained information about

active sites on Pt NPs catalysts when hydrogen is produced. That information will be valuable when designing better catalysts for hydrogen formation in the future. This will also perhaps be applicable for designing better hydrogenation catalysts or any even catalysts for any chemical process in general.

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