Approaching complexity of alkyl hydrogenation on Pd by density-functional modeling

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Abstract. Pd is widely used to catalyse hydrogenation and dehydrogenation reactions. One of them is the hydrogenation of ethylene, which includes the transformation of ethyl species to ethane. Herein, by means of density-functional calculations we address several still insufficiently understood factors affecting the latter process. In particular, we shed light on the following aspects of hydrogenation of alkyls on Pd: *i*) The mechanistic details of how subsurface H accelerates the reaction on (111) surface; *ii*) The role of nanoparticle edges; *iii*) The influence of a common spectator ethylidyne, $\equiv\text{C}-\text{CH}_3$. These factors are identified as significant for the height of the ethyl hydrogenation barrier on Pd. Moreover, we show that butyl hydrogenation on Pd is also governed by very similar interactions, which suggests a broader applicability of our conclusions. This study highlights the complexity of alkyl hydrogenation and analyses the factors that need to be taken into account for a more realistic description of the hydrogenation processes on metal surfaces.

1 Introduction

Pd is a key metal in heterogeneous catalysis. It is a component of pervasive catalysts that transform harmful automotive exhaust gases into non-toxic N_2 and CO_2 .¹ It is also widely used in petroleum cracking reactions² and (de-)hydrogenation of various organic molecules as well as in hydrogen fuel cell technologies.³ Pd can be also used in hydrogen storage materials and hydrogen purification membranes,⁴ because it is able to easily dissociate H_2 on the surface and to absorb large quantities of H in the bulk.^{5,6}

The presence of hydrogen in the subsurface regions can change the catalytic behavior of Pd. For instance, subsurface H is experimentally demonstrated to be crucial for the hydrogenation of alkenes to alkanes, in particular, to its second step, alkyl hydrogenation.⁷⁻¹⁰ Moreover, we calculated the effect of subsurface H on the hydrogenation rates to be by orders of magnitude more pronounced for Pd nanoparticles (NPs) than for extended (111) surface¹¹ in line with experimental observations.¹²

Despite the achieved general understanding of how subsurface H affects ethyl hydrogenation on Pd, many important aspects remain unexplored. For example, it is not clear, whether nanoparticle edge sites are highly active in the hydrogenation or they only facilitate build-up of subsurface H necessary for the high hydrogenation activity of Pd.^{5,9, 13, 14} Another open issue is the effect on the hydrogenation performance of Pd of ethylidyne, $\equiv\text{C}-\text{CH}_3$, which are highly thermodynamically stable species generated from ethylene.¹⁵⁻²¹ Finally, it is important to understand, to what extent the findings obtained for ethyl hydrogenation on Pd are applicable to the hydrogenation of longer alkyls.

To address these issues, we performed comprehensive density-functional studies of hydrogenation reactions on Pd models with different structures and H contents. In particular, we considered the role of various positions of the reacting H with respect to the alkyl species. Next, we comparatively analysed participation of subsurface H in the hydrogenation of ethyl and butyl. We also explored hydrogenation of ethyl on edge sites of Pd nanoparticles. Finally, we investigated kinetic effects of surface ethylidyne species, which are commonly considered mere spectators.

2 Computational

We performed density-functional calculations by means of the plane-wave based Vienna *ab initio* simulation package (VASP)^{22, 23} using a generalized-gradient approximation (GGA) and the exchange-correlation functional PW91.²⁴ The interaction between atomic cores and electrons was described by the projector augmented wave (PAW) method.^{25,26} The Brillouin zone was sampled within the scheme of Monkhorst and Pack.²⁷ To accelerate convergence of electron density, the electron states were smeared using a generalized Gaussian smearing technique²⁸ with the widths of 0.1 and 0.15 eV for nanoparticle and slab models, respectively; the final total energies were extrapolated to the zero smearing. Spin polarization was taken into account only in the calculations of atomic H and ethyl reference species, because according to our tests it negligibly affects the studied reactions. More computational details can be found elsewhere.⁵

Transition state (TS) structures are determined by applying the dimer²⁹ or the climbing-image nudged elastic band (CI-NEB)^{30,31} methods. In the latter case we used eight images of the system to form a discrete approximation of the path between fixed end-points. The TS structures calculated in this way were refined until the forces acting on atoms were all below 2×10^{-4} eV pm⁻¹. The same criterion was applied to the optimization of local minima structures. With a normal-mode analysis we verified for each TS that there is exactly one mode with an imaginary frequency that indicates the relevant C-H bond breaking or formation.

Presented in the following binding energies E_b of adsorbed hydrocarbon and/or adsorbed/subsurface H species were calculated as

$$E_b = E_{\text{ad/sub}} - E_{\text{ad}} - E_{\text{sub}}; \quad (1)$$

there, E_{ad} is the total energy of an adsorbate in the gas phase, E_{sub} is the total energy of the Pd substrate (which may contain ad-/absorbed atoms) and $E_{\text{ad/sub}}$ is the total energy of the substrate with all the ad-/absorbed species in the optimized geometry. With this definition, negative E_b values indicate exothermic interactions. In order to rationalize our findings we analysed^{32,33} various contributions to the binding energy of the reactants on Pd.

The surface of Pd and extended (111) terraces on large Pd NPs were modelled by a five-layer Pd(111) slab with a (3×3) surface unit cell. There all Pd atoms of the three top layers were allowed to relax, whereas atomic positions in the bottom two layers were fixed to yield the computationally optimised nearest-neighbour Pd-Pd distance of 280 pm.³⁴ The vacuum spacing between the repeated slabs was larger than 1 nm. All the calculations were carried out using a 5×5×1 k-point grid.

As a NP model we employed a truncated octahedral particle Pd₇₉ exhibiting (111) facets, each of twelve Pd atoms, and very small (100) facets formed of only four Pd atoms. This NP enables scalable with size (and close to extended systems) quantification of both structural and energetic observables for species adsorbed on their (111) facets.³⁵⁻³⁷ This NP model was also successfully used for studying interactions between much larger Pd NPs³⁸ and in other related density-functional studies.^{14,39-41} In our calculations, Pd₇₉ NP has been positioned in a cubic cell with the lattice parameter $a = 2$ nm, which ensures vacuum spacing of ~1 nm between all atoms in the neighbouring cells. Calculations of the nanoparticle models were performed at the Γ point.

3 Results

3.1 Models for studying hydrogenation reactions on Pd

Surface H atoms in our models are located on three-fold hollow *fcc* sites, which are the most stable positions on Pd(111) surface according to the present calculations, low-energy electron diffraction experiments (at 82 K, when Pd surface is fully covered by H)⁴² and previous calculations.⁴³ In fact, we calculated 9 H atoms on the p(3×3) Pd(111) surface to be by 50 kJ/mol (~6 kJ/mol per H atom) more stable on *fcc* sites than on *hcp* sites.

At higher H pressures not only surface sites, but also certain subsurface sites become occupied by H.⁵ To determine the surface structure at such conditions, we calculated models with all *fcc* or *hcp* surface sites and all octahedral interstitial *oss* or tetrahedral interstitial *tss* and *tss'* subsurface sites occupied by H. The latter sites are below the *fcc*, *hcp* and *top* surface sites, respectively. The *fcc+tss'* configuration is calculated to be by ca. 5 kJ/mol per H atom more stable than the other examined configurations, so we used the *fcc+tss'* configuration in all further calculations of the hydrogenation on Pd, in the models with surface and subsurface

regions covered by H. The tss position is found to be the most stable for subsurface H in the absence of surface species.

When all fcc positions of Pd(111) surface are occupied by H atoms, adsorption of ethylene is blocked. The adsorption is possible only when at least one of the surface fcc sites is available. Another adsorbed H^{fcc} is required to hydrogenate the ethylene molecule to ethyl. Hence, two surface H atoms were missing in our slab and nanoparticle models with ethyl adsorbed on (111) surface or facet. However, at edges of nanoparticles ethylene can adsorb even when all fcc sites are occupied by H atoms. Thus, only one surface H was missing in our models for the hydrogenation at edge sites.

We considered different hydrogen contents employing three types of models for the Pd₇₉ nanoparticle and Pd(111) slab (Fig. 1): (i) *low-coverage* - with just one adsorbed H atom in each model; (ii) *surface-saturated* - with 78 and 7 H atoms, respectively; and (iii) *subsurface-saturated* - with 24 and 9 subsurface H atoms added to the *surface-saturated* models, respectively. In some models (see Sect. 4.5) two adsorbed H atoms were substituted by ethylidyne species to investigate its effect on the hydrogenation of ethyl.

3.2 Ethyl hydrogenation on Pd(111) surface

We first discuss ethyl hydrogenation on Pd(111) surface described by a *low-coverage* model with one H atom per (3×3) surface unit cell. There, we considered for this attacking H^{fcc} atom two initial positions close to the adsorbed ethyl species (see Fig. 2). H^{fcc} atoms in these positions A and B are calculated to be almost equally stable, giving rise to very similar ethyl hydrogenation barriers of 53 and 50 kJ/mol and the reaction exothermicity of -28 and -26 kJ/mol, respectively (Table 1).

The barriers decrease on Pd(111) surface densely covered by H (*surface-saturated* model has 7 H^{fcc} atoms instead of one per (3×3) unit cell), to 47 and 41 kJ/mol for the H^{fcc} attack from sites A and B, respectively (Table 1). The abundance of surface H increases in magnitude the respective reaction energies to -57 and -54 kJ/mol. High loading of subsurface H represented by *subsurface-saturated* models lowers the barriers further, to 42 and 37 kJ/mol, respectively, and makes the reactions ca. 20 kJ/mol more exothermic.

We also explored two scenarios with subsurface H atoms directly attacking the ethyl species. However, we were unable to locate a TS structure corresponding to such

a direct attack. In both scenarios the attacking H atoms were initially located in tss sites below surface Pd atoms C and D (Fig. 2). In the course of TS search, these H^{tss} atoms emerged on the surface in site B, becoming H^{fcc} , and only then attacking the adsorbed ethyl. The first scenario results in higher subsurface to surface migration barrier for H, 37 kJ/mol, and more exothermic hydrogenation reaction, -107 kJ/mol, than the second scenario characterized by 26 and -96 kJ/mol, respectively. Two scenarios yielded similar hydrogenation barriers of ~35 kJ/mol, i.e. only marginally lower than when H^{fcc} attacks ethyl directly.

The variations in activation energies are also reflected in the geometries of transitions states. The forming C-H bond elongates in the TSs with the increased number of H atoms in the surface and subsurface regions, from ~160 pm in the *low-coverage* models to ~170 pm in the *subsurface-saturated* models. Hence, the transition states become earlier with increasing H loading. C-H distances in the TS structures linearly correlate with the reaction barriers (Fig. 3). The Pd-C bonds elongate from 222-223 pm at low-coverage to 226-231 pm at high H content, because ethyl becomes weaker bound when concentration of H increases.

We also studied how ethylidyne species can modify ethyl hydrogenation barriers on Pd(111) surface. In these models two ethylidyne molecules were present in p(3×3) Pd(111) supercell (Fig. 4), and the attacking H was in the position B. In the *low-coverage* and *surface-saturated* situations, ethylidyne lowers the ethyl hydrogenation barrier by 6 kJ/mol to 44 and 35 kJ/mol, respectively (Table 1). When subsurface region is also saturated by H ethylidyne lowers the barrier to only 28 kJ/mol, which is the lowest barrier that we could obtain on Pd(111) surface. The presence of ethylidyne also makes the reaction more exothermic by 29, 49, and 44 kJ/mol in the three above mentioned cases, respectively.

3.3 Ethyl hydrogenation on Pd₇₉ particle

We begin with results calculated for ethyl hydrogenation on {111} facets of Pd₇₉ nanoparticles at varying H content. For *low-coverage* NP model (Fig. 1), the activations barrier of 54 kJ/mol and the reaction energy of -13 kJ/mol were obtained (Table 2). The barrier decreases by 8 kJ/mol and the reaction becomes by almost 40 kJ/mol more exothermic in the *surface-saturated* model. Notably, for *subsurface-saturated* NPs the barrier is only ca. 15 kJ/mol, slightly depending on whether the attacking H originates from the surface or subsurface regions. Similarly to the Pd(111) slab model (see Section 3.2), our attempts to find direct hydrogenation pathway for

subsurface H reactant failed: the attacking subsurface H had to be stabilized on the surface before starting to react.

Ethyl hydrogenation at edges between {111} facets in the *low-coverage* models is characterized by the barrier of 42 kJ/mol and minor exothermicity (Table 2). In the *surface-saturated* NP model the barrier becomes higher by 7 kJ/mol and the reaction is noticeably exothermic, -34 kJ/mol. In the *subsurface-saturated* NP (Fig. 4) the barrier decreases to 33 kJ/mol and the reaction becomes 20 kJ/mol more exothermic than without subsurface H. We also calculated a model with 42 H^{tss} atoms, where additional H atoms are beneath Pd atoms of two {111} facets separated by the edge where ethyl species is adsorbed. The added H^{tss} atoms increase the reaction exothermicity by 51 kJ/mol, but only slightly decrease the barrier. The large exothermicity can be partly assigned to emerging of one subsurface H^{tss} atom on the surface during the hydrogenation reaction.

The presence of two ethylidyne species on (111) terrace of Pd₇₉ NP affected the hydrogenation of ethyl in the following way. At low H coverage the barrier changes only insignificantly, by 2 kJ/mol, when two ethylidyne molecules are co-adsorbed on the facet where ethyl is located. Two ethylidyne co-adsorbates make the reaction more exothermic by 32 kJ/mol. In the *surface-saturated* model of Pd₇₉ the ethylidyne species decrease the hydrogenation barrier by 9 kJ/mol and strongly increase the reaction exothermicity. At variance, in the *subsurface-saturated* NP model two ethylidyne co-adsorbates increase the ethyl hydrogenation barrier by 15 kJ/mol, while hardly increasing the reaction exothermicity.

4 Discussion

At low H coverage the barriers for ethyl hydrogenation are essentially identical on Pd(111) slab model and terrace of a {111} facet of Pd₇₉ nanoparticle, 50- 54 kJ/mol (Tables 1 and 2). On the surface covered by H the barriers decrease by 6-9 kJ/mol. In the presence of also subsurface H atoms, the barriers decrease further, but by different value: by only ~5 kJ/mol on Pd(111) slab (Table 1), but by at least 30 kJ/mol on Pd₇₉ nanoparticle (Table 2).

4.1 Analysis of contributions to the binding and activation energies

Binding energy of the attacking H linearly correlates with the barrier for ethyl hydrogenation.¹¹ The barrier decreases because the subsurface H atoms destabilize the adsorbed H atoms and make them more reactive via partial occupation of the anti-bonding H1s-Pd4d states. Such destabilization is much more pronounced on the NP models.

To understand this effect in detail and quantify it we analyzed the binding energy (E_b) of the interacting fragment (ethyl and attacking H atom) in the initial (IS) and transition state (TS) structures (Table S1 in ESI). Here E_b is a stability indicator of the IS and TS and the difference between E_b values in these systems equals the hydrogenation barrier. We found that both binding energies decrease with increasing the H loading, which indicates that IS and TS are concomitantly destabilized (Table S1 in ESI). However, E_b of ethyl and H in the IS structures decrease more than those in the TS. Hence, with increasing the H loading IS are destabilized more than TS and hydrogenation barriers are lowered.

We decomposed binding energies of initial and transition states into various contributions^{44,45} (Table S1 in ESI):

$$E_b = E_{\text{int}} + E_d(\text{Pd}) + E_d(\text{ethyl}) + E_{\text{coads}} \quad (2)$$

E_{int} is the energy of the (full) interaction of metal with reactants, Pd-(ethyl+H), calculated as

$$E_{\text{int}} = E_{\text{ad/sub}} - E_{\text{ad}}^{\text{sp}} - E_{\text{sub}}^{\text{sp}}. \quad (3)$$

Here $E_{\text{ad}}^{\text{sp}}$ and $E_{\text{sub}}^{\text{sp}}$ are energies of the isolated adsorbate (i.e. $\text{C}_2\text{H}_5+\text{H}$) and substrate parts obtained in a single-point fashion using the geometry of the combined “ad/sub” system. In turn,

$$E_d(\text{ethyl}) = E_{\text{ethyl}}^{\text{sp}} - E_{\text{ethyl}}, \quad (4)$$

$$E_d(\text{Pd}) = E_{\text{sub}}^{\text{sp}} - E_{\text{sub}} \quad (5)$$

are energies required to deform separated C₂H₅ or Pd from their equilibrium structures to the structures they exhibit in the adsorption complex. One more contribution,

$$E_{\text{coads}} = E_{\text{ad}}^{\text{sp}} - E_{\text{ethyl}}^{\text{sp}} - E_{\text{H}}, \quad (6)$$

needs to be added, which takes into account the interaction between ethyl species and attacking H atom. The analysis of the E_{b} contributions (Table S2 in ESI) can clarify, which of them influence the barriers and how, since

$$\Delta E^{\ddagger} = \Delta E_{\text{b}} = \Delta E_{\text{int}} + \Delta E_{\text{d}}(\text{Pd}) + \Delta E_{\text{d}}(\text{ethyl}) + \Delta E_{\text{coads}}. \quad (7)$$

It is also interesting to identify, which contributions control the trend of hydrogenation barriers lowering with increasing surface and subsurface H concentration.

E_{int} defined in (3) characterizes the strength of metal-adsorbate interaction. Since C₂H₅ and H in the IS interact with the catalyst much stronger than the essentially unbound C₂H₆ product does, increase of $\Delta E_{\text{int}} = E_{\text{int}}(\text{TS}) - E_{\text{int}}(\text{IS})$ strongly increases the barrier height, and ΔE_{int} values are as high as 213-343 kJ/mol. ΔE_{int} decreases with increasing H loading, because both the magnitude of $E_{\text{int}}(\text{IS})$ decreases and $E_{\text{int}}(\text{TS})$ values tend to increase in magnitude with increasing H loading, since TSs become earlier with the H loading. As a result C-H distances in the TS structures linearly correlate with the reactions barriers (Fig. 3, $R^2 = 0.95$), like the ΔE_{int} values do (Fig. 5, $R^2 = 0.97$).

The deformation energy values (4,5) are significantly (by one order of magnitude) smaller than the other two contributions E_{int} and E_{coads} . Pd substrate is deformed by 9-24 kJ/mol more strongly in the IS structures than in the partially desorbed TS structures, and the difference increases when subsurface H is added. The deformation of ethyl follows the opposite trend, i.e. the hydrocarbon species are stronger deformed in the TS structure than in the IS because the C atom of ethyl becomes five coordinated (more distorted) in the TS structure, but the associated energies are minor, 1-4 kJ/mol.

Overall, the co-adsorption contribution, E_{coads} (6), strongly lowers the barriers. One of the reasons is that reactants repulse each other in the IS structure, destabilizing all ISs by 8-15 kJ/mol. On the contrary, in the TS the E_{coads} interaction is strongly attractive, $-259 \div -209$ and $-274 \div -175$ kJ/mol, for the slab and nanoparticle models, respectively, reflecting the

formation of C-H bond. When the TS structures become earlier at increasing H loading, ΔE_{coads} linearly decreases with elongation of the forming bond (Fig. 6, $R^2 = 0.956$).

Comparing energy contributions to the activation barriers of various systems (7), one can gain insight into the mechanisms enhancing the hydrogenation activity of Pd. It is not surprising that increase of E_{int} values strongly increases hydrogenation barriers as it describes the cleavage of H-Pd and C-Pd bonds, whereas E_{coads} strongly decreases the barriers as it describes the forming C-H bond. Since the products desorb from the surface the $E_{\text{d}}(\text{Pd})$ contribution also decreases the barrier, while the effect of the $E_{\text{d}}(\text{ethyl})$ is opposite, but rather minor. With increasing H loading the TSs become earlier, hence the ΔE_{int} contribution lowers the barrier, while $\Delta E_{\text{d}}(\text{Pd})$ and ΔE_{coads} increase it. Since ΔE_{int} decreases faster than $\Delta E_{\text{d}}(\text{Pd})$ and ΔE_{coads} with growing H content, the hydrogenation barrier also decreases. For instance, ΔE_{int} and ΔE_{coads} decrease in magnitude by 81 and 55 kJ/mol, respectively, when subsurface H is introduced in the Pd₇₉ NP. Hence, the difference between contributions $\Delta E_{\text{int}} + \Delta E_{\text{coads}}$ is 26 kJ/mol and it leads to the reduction of the barrier by essentially the same value, 30 kJ/mol. However, when subsurface H is introduced in the Pd(111) slab model, ΔE_{int} decreases in magnitude by only 22 kJ/mol, whereas ΔE_{coads} decreases in magnitude by 30 kJ/mol. Hence, the presence of subsurface H increases $\Delta E_{\text{int}} + \Delta E_{\text{coads}}$ by 8 kJ/mol, when the attacking H is in position B. Therefore, based only on the $\Delta E_{\text{int}} + \Delta E_{\text{coads}}$ value one should expect that subsurface H would increase the hydrogenation barrier. However, in this case the $\Delta E_{\text{d}}(\text{Pd})$ contribution is 11 kJ/mol and it reverses the trend. Thus, subsurface H lowers the hydrogenation barrier on the NP model due to $\Delta E_{\text{int}} + \Delta E_{\text{coads}}$ contributions, while in slab models the deformation of the metal is also important and has to be taken into account.

4.2 Reactivity of {111} terrace sites on Pd₇₉

At low hydrogen coverage the edge sites of the Pd₇₉ NP adsorb ethyl species by 14 kJ/mol stronger compared to the terrace sites. Adsorption of ethyl in the edge position also lowers its hydrogenation barrier to 42 kJ/mol from 54 kJ/mol found on the terrace. Surface saturation by H has an opposite effects on the terrace and edge hydrogenation barriers, making them almost equal, ~47 kJ/mol. In turn, subsurface H notably lowers these barriers to 16 and 33 kJ/mol, respectively. When one more surface H atom is removed in the case of ethyl species in edge position to obtain a system with the same number of H atoms, 78 H^{fcc} and 24 H^{tss}, as in the case of the terrace reaction, the ethyl

hydrogenation barrier changes by only 3 kJ/mol. Thus, nanoparticle edges may (at low surface H coverage) or may not (at high surface H coverage and presence of subsurface H) be more active in the hydrogenation than the terrace sites depending on the reaction conditions.

The above mentioned findings can be rationalized by the varying magnitude of binding energies of ethyl species and steric repulsion between co-adsorbed species in the IS structures. For instance, in the *subsurface-saturated* models IS structure with terrace ethyl species is less stable by 31 kJ/mol than the corresponding structure with ethyl species at the NP edge (Table S3 in ESI). The reason for this result is weaker binding of the ethyl species and stronger ethyl-H repulsion in the IS structure with terrace ethyl species. In the TS structures the interaction between co-adsorbates starts to change from lateral repulsion to attraction due to the formation of C-H bond and the energy difference between edge and terrace TS structures becomes only 18 kJ/mol. So the barrier is decreased by 13 kJ/mol, when ethyl is at terrace instead of edge sites. When ethane molecule is formed, the interaction between ethyl and H is only due to the C-H bond formation. Hence, the reaction energies notably depend on whether the ethyl species is located on the terraces or edges, -98 or -54 kJ/mol, respectively.

4.3 Butyl hydrogenation

The barrier of 2-butyl hydrogenation on Pd(111) slab model at low H coverage, 59 kJ/mol, is slightly higher than that of ethyl hydrogenation, 53 kJ/mol, while the reaction is more exothermic by 13 kJ/mol. On *surface-saturated* and *subsurface-saturated* Pd₇₉ NP models the corresponding calculated barriers, 53 and 21 kJ/mol, are higher by 7 and 5 kJ/mol than the barriers for ethyl hydrogenation. Hence, we can conclude that the hydrogenation barriers slightly increase, when the hydrocarbon chain is elongated, but the qualitative results calculated for the shorter alkyl fragment do not alter.

4.4 Effects of ethylidyne

The influence of the adsorbed ethylidyne species on the ethyl hydrogenation is calculated to be very similar on Pd NP and slab models (Tables 1 and 2). In all studied cases, with one exception, the presence of ethylidyne species slightly decreases the barriers by 2-9 kJ/mol with respect to the corresponding models without ethylidyne

species. Interestingly, in the presence of ethylidyne covering of the surface by H reduces the barriers by 9 and 15 kJ/mol, respectively, for the slab and NP models, while the subsurface H causes additional lowering of the barriers by 6-7 kJ/mol. Hence, it seems that the presence of ethylidyne species promotes the effect of the surface H^{fcc} atoms and suppresses the effect of the subsurface H^{tss} on the hydrogenation barrier.

5 Summary

We modeled the prototypic alkyl hydrogenation reaction, ethyl hydrogenation to ethane, on Pd and explored the role of the following factors on the reaction: the size of Pd particles (large particles were approximated by Pd(111), while nano-effects were traced by the Pd₇₉ NP model), nanoparticle edges, the concentration of surface and subsurface H, the length of the alkyl chain, as well as presence of co-adsorbed ethylidyne species. The main results of this work can be summarized as follows:

(i) Hydrogen loading effect on Pd(111) and Pd₇₉. We found that the hydrogenation barriers decrease at increased H loading, because the latter destabilizes initial states more than transition states. In particular, subsurface H saturation makes the barrier lower than 20 kJ/mol on Pd₇₉ nanoparticle. Further analysis showed that full interaction energies of reactants with the metal substrate and their co-adsorption energies govern the calculated decrease of hydrogenation barriers in the presence of subsurface H, especially on Pd₇₉ NP. In the case of Pd(111) single crystal, the mechanical rigidity of the substrate also contributes to decreasing the barrier height.

(ii) Ethyl versus butyl. The elongation of the hydrocarbon chain from ethyl to butyl consistently increases the hydrogenation barriers by up to 7 kJ/mol. The essential independence of such increase on the catalysts structure suggests that the most general conclusions derived from the simulated hydrogenation of ethyl are also applicable to somewhat longer alkyls.

(iii) Pd₇₉ terrace versus edge. The effect of H loading on the barrier heights is not straightforward for ethyl located at edge sites of the Pd₇₉ nanoparticle. At low H loading the barrier at edges is by ~10 kJ/mol lower than that for ethyl hydrogenation on terrace site. However, when surface is covered by H the barrier for ethyl hydrogenation at edge site increases by 7 kJ/mol (while barrier at terrace sites slightly decrease) and the heights of these barriers become comparable. The presence of subsurface H notably lowers the ethyl hydrogenation barrier at edge sites, to ~30 kJ/mol.

(iv) Ethylidyne species. The presence of ethylidyne is calculated to decrease the hydrogenations barriers of ethyl by up to 10 kJ/mol on both Pd(111) slab and Pd₇₉ models. Only when surface and subsurface regions of Pd₇₉ NP are covered by H, ethylidyne species were acting to increase the barrier. More work is required to further deepen our understanding of the influence of such strongly bound spectator species as ethylidyne on the kinetic of hydrogenation of olefins.

To conclude, we demonstrated that various surface species and structural features of the catalysts can affect the hydrogenation of ethyl on Pd, as well as quantified and rationalized these effects. Our findings illustrate the complexity of even the simplest alkyl hydrogenation reaction on transition metal catalysts and justify the necessity of developing sufficiently realistic modelling strategies in heterogeneous catalysis.

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Figure 1. Cross-sections of the studied H/Pd catalyst models. Colours used: surface Pd atoms – turquoise; interior Pd atoms – cyan; surface H – pink, subsurface H – red.

Figure 2. Positions of the attacking H atoms in the initial state containing ethyl + 7 H^{fcc} + 9 H^{tss} on Pd(111) surface: A, B - surface fcc positions; C, D - subsurface tss positions, from where H^{tss} moves first on the surface to position B and then as H^{fcc} it attacks the ethyl species. Colours used: Pd atoms – turquoise; C – gray; surface H – pink, H in hydrocarbons – white.

Figure 3. Activation barriers of ethyl hydrogenation as a function of the length of the C-H bond that is created in the transition state ($y = -1.6x + 302.8$; $R^2 = 0.95$).

Figure 4. Sketches of the optimised initial, transition and final state structures for ethyl hydrogenation on Pd(111) surface and Pd₇₉ particle. Figure columns (from left to right): Pd(111), Pd(111) with pre-adsorbed ethylidyne, terraces of Pd₇₉, edges of Pd₇₉, terraces of Pd₇₉ with pre-adsorbed ethylidyne. All substrates are saturated by surface and subsurface H (see text). Pd – turquoise, C – gray, surface H – pink, H in hydrocarbons – white; attacking H is highlighted.

Figure 5. ΔE_{int} defined in (3) as a function of C-H distances of the bond that is created in the TS during the hydrogenation process ($y = -4.8x + 1094$; $R^2 = 0.97$).

Figure 6. ΔE_{coads} defined in (6) as a function of C-H distances of the bond in the TS that is created during the hydrogenation process ($y = 3.6x - 840.9$; $R_2 = 0.96$).

Table 1. Activation ($\Delta E^\ddagger$, kJ/mol) and reaction energies (ΔE , kJ/mol) calculated for Pd(111) slab model. Selected interatomic distances (in pm) in the TS structures are also given. H^{fcc} and H^{tss} label surface and subsurface H atoms in the *fcc* and *tss* positions, respectively.

H ^a	Elementary reaction	$\Delta E^\ddagger$	ΔE	C-H	Pd-C	H-Pd
A	$C_2H_5 + H^{fcc} \rightarrow C_2H_6$	53	-28	159	222	169, 191, 255
A	$C_4H_9 + H^{fcc} \rightarrow C_4H_{10}$	59	-41	158	237	168, 188, 277
B	$C_2H_5 + H^{fcc} \rightarrow C_2H_6$	50	-26	160	223	170, 184, 266
A	$C_2H_5 + 7 H^{fcc} \rightarrow C_2H_6 + 6 H^{fcc}$	47	-57	165	227	170, 183, 242
B	$C_2H_5 + 7 H^{fcc} \rightarrow C_2H_6 + 6 H^{fcc}$	41	-54	163	227	172, 198, 207
A	$C_2H_5 + 7 H^{fcc} + 9 H^{tss} \rightarrow C_2H_6 + 6 H^{fcc} + 9 H^{tss}$	42	-79	169	227	171, 183, 231
B	$C_2H_5 + 7 H^{fcc} + 9 H^{tss} \rightarrow C_2H_6 + 6 H^{fcc} + 9 H^{tss}$	37	-75	170	226	171, 191, 224
C-B	$C_2H_5 + 7 H^{fcc} + 9 H^{tss} \rightarrow C_2H_5 + 8 H^{fcc} + 8 H^{tss}$	37 ^b	1			
B	$C_2H_5 + 8 H^{fcc} + 8 H^{tss} \rightarrow C_2H_6 + 7 H^{fcc} + 8 H^{tss}$	35 ^c	-107	170	231	173, 191, 203
D-B	$C_2H_5 + 7 H^{fcc} + 9 H^{tss} \rightarrow C_2H_5 + 8 H^{fcc} + 8 H^{tss}$	26 ^b	-14			
B	$C_2H_5 + 8 H^{fcc} + 8 H^{tss} \rightarrow C_2H_6 + 7 H^{fcc} + 8 H^{tss}$	36 ^c	-96	170	230	173, 200, 202
B	$C_2H_5 + H^{fcc} + 2 CCH_3 \rightarrow C_2H_6 + 2 CCH_3$	44	-57	164	225	170, 185, 232
B	$C_2H_5 + 5 H^{fcc} + 2 CCH_3 \rightarrow C_2H_6 + 2 CCH_3 + 4 H^{fcc}$	35	-103	167	229	172, 199, 201
B	$C_2H_5 + 5 H^{fcc} + 2 CCH_3 + 9 H^{tss} \rightarrow C_2H_6 + 2 CCH_3 + 4 H^{fcc} + 9 H^{tss}$	28	-119	172	228	173, 197, 198

^a Initial position of the attacking H atom (according to Figure 2) or change in the position is shown; ^b Barrier for diffusion of H from subsurface region to the surface; ^c Barrier for ethyl hydrogenation from the initial structure with the attacking H atom located at the surface.

Table 2. Activation ($\Delta E^\ddagger$, kJ/mol) and reaction energies (ΔE , kJ/mol) calculated for Pd₇₉ nanoparticle model. Selected interatomic distances (in pm) in the TS structures are also given. H^{fcc} and H^{tss} label surface and subsurface H atoms in the *fcc* and *tss* positions, respectively.

Ethyl ^a	Elementary reaction	$\Delta E^\ddagger$	ΔE	C-H	Pd-C	H-Pd
terrace	$C_2H_5 + H^{fcc} \rightarrow C_2H_6$	54	-13	157	222	170, 185, 272
terrace	$C_2H_5 + 78 H^{fcc} \rightarrow C_2H_6 + 77 H^{fcc}$	46	-52	165	227	171, 185, 234
terrace	$C_4H_9 + 78 H^{fcc} \rightarrow C_4H_{10} + 77 H^{fcc}$	53	-53	163	236	168, 184, 286
terrace	$C_2H_5 + 78 H^{fcc} + 24 H^{tss} \rightarrow C_2H_6 + 77 H^{fcc} + 24 H^{tss}$	16	-98	182	224	172, 191, 201
terrace	$C_2H_5 + 79 H^{fcc} + 23 H^{tss} \rightarrow C_2H_6 + 78 H^{fcc} + 23 H^{tss}$	14	-109	182	227	172, 195, 200
terrace	$C_4H_9 + 78 H^{fcc} + 24 H^{tss} \rightarrow C_4H_{10} + 77 H^{fcc} + 24 H^{tss}$	21	-101	179	234	170, 191, 211
terrace	$C_2H_5 + H^{fcc} + 2 CCH_3 \rightarrow C_2H_6 + 2 CCH_3$	52	-45	164	222	165, 196, 276
terrace	$C_2H_5 + 76 H^{fcc} + 2 CCH_3 \rightarrow C_2H_6 + 75 H^{fcc} + 2 CCH_3$	37	-103	166	227	172, 182, 269
terrace	$C_2H_5 + 76 H^{fcc} + 24 H^{tss} + 2 CCH_3 \rightarrow$ $C_2H_6 + 75 H^{fcc} + 24 H^{tss} + 2 CCH_3$	31	-101	177	224	168, 193, 238
edge	$C_2H_5 + H^{fcc} \rightarrow C_2H_6$	42	-4	159	219	169, 183, 305
edge	$C_2H_5 + 79 H^{fcc} \rightarrow C_2H_6 + 78 H^{fcc}$	49	-34	163	224	169, 193, 232
edge	$C_2H_5 + 79 H^{fcc} + 24 H^{tss} \rightarrow C_2H_6 + 78 H^{fcc} + 24 H^{tss}$	33	-54	169	224	170, 198, 226
edge	$C_2H_5 + 79 H^{fcc} + 42 H^{tss} \rightarrow C_2H_6 + 78 H^{fcc} + 42 H^{tss}$	29	-105	177	225	169, 192, 273

^a Location of ethyl species on the NP.

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