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Co-adsorption of Butadiene and Hydrogen on the (111) Surfaces of Pt and Pt_2Sn Surface Alloy: Understanding the Co-habitation from First Principles Calculations

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Abstract
Co-adsorption is a key initial step in heterogeneous catalysis, which by bringing the reactants together at high coverage on the surface of the catalyst has a clear implication on the catalytic reaction activity. We show that when using Density Functional Theory (DFT) calculations, the choice of the exchange correlation functional can have a qualitative influence on the nature of the obtained most stable coadsorption state. The coadsorption of butadiene and hydrogen, the precursor state for catalytic hydrogenation, is studied on Pt(111) and on the surface alloy Pt_2Sn/Pt(111). At typical hydrogenation conditions, the PBE exchange correlation functional gives as most stable situation on both model catalysts a surface fully covered with hydrogen, butadiene remaining in gas phase. This behavior does not agree with available experimental data, and results from an incorrect balance between H and butadiene adsorption energy, mainly by a poor description of dispersion energy for butadiene adsorption. The non-local optPBE-vdW functional provides opposite and correct results, with a co-adsorption of butadiene and hydrogen as most stable situation. The butadiene adsorption energy is strengthened by the description of dispersive forces, hence modifying the nature of the energetic competition between the two adsorbates. The co-asorption energy difference between PBE and optPBE-vdW amounts to 1.04 (resp. 0.7) eV for Pt(111) (resp. Pt_2Sn/Pt(111)) on the considered 3x3 unit cell. The computational study of co-adsorption systems from DFT is hence delicate. Errors do not only impact the quantitative adsorption energy of one adsorbate, but they might cumulate over several species, finally providing a qualitatively wrong picture of the optimal co-adsorption situation. Going beyond the standard Generalized Gradient Approximation hence appears mandatory for a correct description of catalytic reactivity of unsaturated hydrocarbons.

1- Introduction

Catalytic hydrogenation plays a major role in chemistry, for example in petrochemistry and in food chemistry, and it has been deeply investigated both experimentally and theoretically.[1] Pt and Pt group metals are commonly used as catalysts for these hydrogenation reactions. Pioneering works of Sabatier, Langmuir and

Hinshelwood have shown that the initial chemisorption of reactants, unsaturated molecule and hydrogen, are key steps for the reaction.[2,3] According to the Langmuir-Hinshelwood mechanism, atomic hydrogen and the unsaturated molecule need to be simultaneously adsorbed on the surface of the catalysts for the hydrogenation reaction to occur. It is hence of great importance to understand in details the adsorption competition between hydrogen and butadiene.

Several experimental studies considered the co-adsorption of unsaturated molecules, like ethene, and hydrogen at low coverage, but in such case no specific interaction was noted.[4,5,6,7] When higher H coverage is induced, close to one monolayer (one H per surface Pt atom), then strong consequences occur. Benzene adsorption on Pt(111) is completely blocked when a pre-adsorption of H is realized at saturation coverage.[8] Zhao et al have studied the influence of prior hydrogen adsorption on the chemisorption and hydrogenation of butadiene on a Pt(111) surface using ultra high vacuum (UHV) surface science techniques.[9] They showed that H adsorption blocks sites for butadiene adsorption, with a linear decrease of butadiene coverage upon H pre-adsorption and a complete blockage of molecular adsorption at monolayer (i.e. saturation) H coverage. It is striking that if hydrogen and butadiene are coadsorbed on Pt(111) at low pressure and low temperature then, upon heating up in a temperature programmed desorption (TPD) experiment, no hydrogenation product is formed. Hence, not only co-adsorption is important, but the evolution of the surface population as a function of reaction condition, temperature and reactant partial pressures is key to control the activity.

First principle calculations can bring important insights on the co-adsorption process of hydrogen and unsaturated molecules on a transition metal surface. However, most of the theoretical approaches have been performed at low coverage, a situation where only a few hydrogen atoms are placed on the surface.[10,11,12] Lateral interactions between hydrogen and molecules are hence small or ignored. Three recent studies from computations need however to be underlined. Chizallet et al have studied in details the adsorption of butadiene and butene in the presence of chemisorbed hydrogen atoms on the Pd(111) and Pd(100) surfaces, determining the most stable co-adsorption situation as a function of partial pressures and temperature.[13] The calculations were performed with the semi-local PW91 exchange-correlation functional. They showed a marked decrease of butadiene adsorption energy as a function of hydrogen pre-coverage. At realistic hydrogen pressure (~1 bar), the most stable Pd(111) surface is fully covered with hydrogen and the unsaturated molecule does not adsorb, whatever the temperature and butadiene partial pressure (in the considered range lower than 10 bar). Adsorption of butadiene becomes competitive only if the partial pressure of hydrogen is reduced to 10^{-3} bar. This contrasts with the usual Langmuir-Hinshelwood picture that requires for hydrogenation that both the unsaturated hydrocarbon molecule and hydrogen atoms are adsorbed on the surface. Hence this computational result requires confirmation or would suggest to revise major aspects of the butadiene hydrogenation mechanism. Canduela-Rodriguez et al studied benzene hydrogenation in conditions of pressure and temperature relevant to industrial conditions.[14] In the same study they described the co-adsorption of benzene and hydrogen at high coverage conditions, comparing semi-local and van der Waals type functional. They noted a decrease in benzene adsorption energy with increasing hydrogen coverage. At hydrogen coverage higher than 0.67 ML, benzene is not chemisorbed any more, but only weakly physisorbed at larger distance from the surface. As a result, the adsorption energy is

markedly decreased. At realistic hydrogen pressure, typical to hydrogenation conditions, the hydrogen coverage is found to be high (0.89 or 1 ML) and the benzene molecule is only weakly physisorbed. It should be noted that benzene is constrained to be present (physisorbed or chemisorbed) at a coverage of 0.11 ML in this study and that situations where the surface is only populated by hydrogen are not considered in the thermodynamic diagrams. Very recently Fergusson et al studied the co-adsorption of hydrogen and guaiacol on Pt(111) using a van der Waals-corrected DFT functional, and they showed that at conditions relevant to hydrotreatment, the surface is covered by a monolayer of H atoms, while guaiacol is only physisorbed on top of this layer.[15]

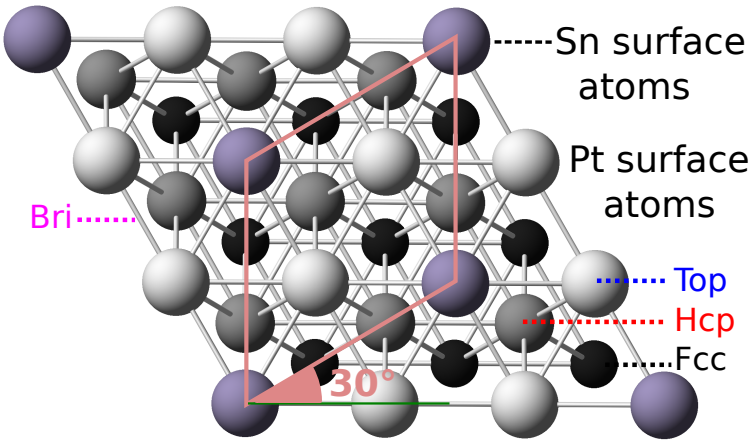
Besides catalytic activity, selectivity in targeted products is also crucial. Pt is a very active catalyst for the hydrogenation of unsaturated molecules, however in the case of di-olefins as butadiene, it leads to a mixture of partially hydrogenated butenes and totally hydrogenated butane. The butenes are the valuable products so that increasing the selectivity of their formation is an important target. Adding main group metals as Sn is a general strategy to improve the selectivity of Pt for partial hydrogenation of the unsaturated molecule.[16] Sn forms a surface alloy on Pt, and two superstructures have been seen, $(\sqrt{3}\times\sqrt{3})R30°$ and 2×2. We have shown in previous studies that Sn is unable to bind with H or with the unsaturated molecule but promotes a partial electron transfer towards Pt.[17,18] That electron enrichment leads to a weakening of the interaction between the Pt sites and both butadiene and hydrogen and opens selective pathways for butadiene hydrogenation.[19] The influence of the Pt-Sn surface alloy on the coadsorption of the reactants at realistic H coverage was, however, not addressed from the computational viewpoint.

The coadsorption between the unsaturated molecule and hydrogen at realistic pressure and temperature on the (111) surfaces of Pt and of the surface alloy with Sn hence still offers several open questions. It is indeed unclear how the two reactants that are of very different size compete for adsorption. The molecular chemisorption energy of butadiene on Pt(111) (1.89 eV with the PBE functional) is much larger than the dissociative chemisorption energy of hydrogen (0.52 eV for ½ H_2 forming one surface hydrogen atom), but the relevant quantity is the adsorption energy per unit surface for the saturation coverage. Very different saturation coverage values are obviously obtained for H and butadiene. In addition, it has been underlined recently that various exchange correlation functionals, including or not van der Waals contributions, can give significantly different values for the chemisorption of unsaturated molecules.[20] It is hence important to determine whether these functionals give a similar or different qualitative picture for the chemisorption of a mixture of butadiene and hydrogen in relevant conditions for catalysis.

In this paper we study, from a DFT approach, the coadsorption of butadiene and hydrogen on Pt and Pt-Sn surface alloy, focusing on the influence of hydrogen coverage in realistic temperature and pressure conditions. We will focus on the case of the (111) surfaces, as a typical stable and dominant termination for Pt and it surface alloys, but the concept developed are qualitatively extendable to other Pt terminations as well as other metal catalysts or other unsaturated molecules.

2- Models and methods

We have considered two models for the hydrogenation catalyst: a Pt(111) surface and a Pt-Sn surface alloy formed by a single layer of Pt_2Sn composition in epitaxy on Pt(111), noted Pt_2Sn/Pt(111).[21,22] The Sn atoms are positioned in the surface layer, and we consider here the case of the $(\sqrt{3}\times\sqrt{3})R30°$ supercell corresponding to a 1/3 ML coverage of Sn (see scheme 1).



Scheme 1: Top view of a (3×3) representation of the Pt_2Sn/Pt(111) surface with a Pt_2Sn first layer stoichiometry; surface Sn (resp. Pt) is shown as a purple (resp. light gray) ball, while Pt atoms in the second (resp. third) layers are shown with smaller dark grey (resp. black) balls. The pink cell shows the primitive surface alloy super-cell $(\sqrt{3}\times\sqrt{3})R30°$.

The pure Pt(111) surface was modeled by a (3×3) supercell. Since the saturation coverage for butadiene on Pt(111) is 0.15 ML, we have considered two coverage values for butadiene: 1/9 ML and zero.[9] The periodic DFT calculations were performed using two different exchange correlation functionals. One standard semi-local Generalized Gradient Approximation functional was used (PBE) as it has been previously employed in a large number of adsorption studies on metal.[23] As indicated above, a detailed comparison with single crystal adsorption calorimetry recently showed that the chemisorption energy of unsaturated hydrocarbon molecules was underestimated with PBE and better described with the non-local optPBE-vdW functional, that takes into account dispersion interactions. The latter was developed within the formalism of Dion et al by adding a non-local correlation term to a re-optimized PBE GGA exchange functional.[24,25] Hence, the optPBE-vdW functional was also used and the results were compared to those obtained with PBE. The optimized platinum lattice constant is 2.814 Å (resp. 2.821 Å) with PBE (resp. optPBE-vdW) and the very small difference implies that lattice strain does not play an important role in chemisorption energy differences.

3- Results and discussion

3.1- Adsorption of hydrogen on Pt(111)

The potential energy surface of an hydrogen atom on Pt(111) is very flat with only a weak preference for the fcc hollow site (by only 0.05 eV at 0.25 ML coverage) with the PBE functional. Diffusion of H on the Pt(111) surface will hence be very easy. The stability

comparison between sites is unchanged when increasing the coverage. Until 1ML, the most stable configuration corresponds to the occupation of the fcc hollow sites, with a weak repulsive lateral interaction of 0.07 eV per H atom at 1ML. Above 1ML, the most stable structures mix fcc hollow and top sites. These structures are however metastable compared to the 1ML situation and hence will not be associated to any stability domain in the surface stability diagram. Penetration of the H atom in the subsurface Pt layer is unstable. The small preference for the fcc hollow site is changed with the optPBE-vdW functional, and the top site becomes slightly more stable than the fcc site (by 0.04 eV at 0.25 ML coverage). The H adsorption energy is smaller with optPBE-vdW than with PBE (at 1/9 ML coverage with a ½(H_2) reference: -0.53 eV for PBE and -0.42 eV for optPBE-vdW). The optPBE-vdW value appears more accurate in comparison with the calorimetry value (-0.37 eV).[20] The most stable structures at higher coverage for the optPBE-vdW functional are formed by top site H atoms. The lateral repulsion at 1ML is 0.08 eV, very close to the PBE value.

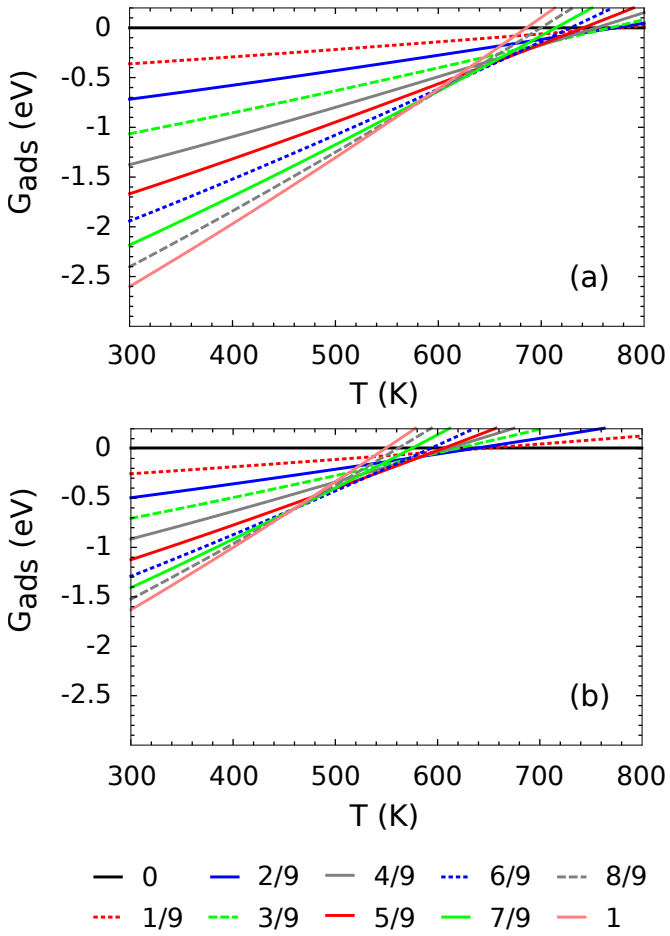


Figure 1: Adsorption free energy of hydrogen on Pt(111) for P_{H2}=1 bar as a function of the temperature for the PBE functional (a) and the optPBE-vdW functional (b), for various values of the coverage in ML. The adsorption free energy is normalized to a (3×3) surface cell, i.e. corresponds to 9 H atoms at 1ML.

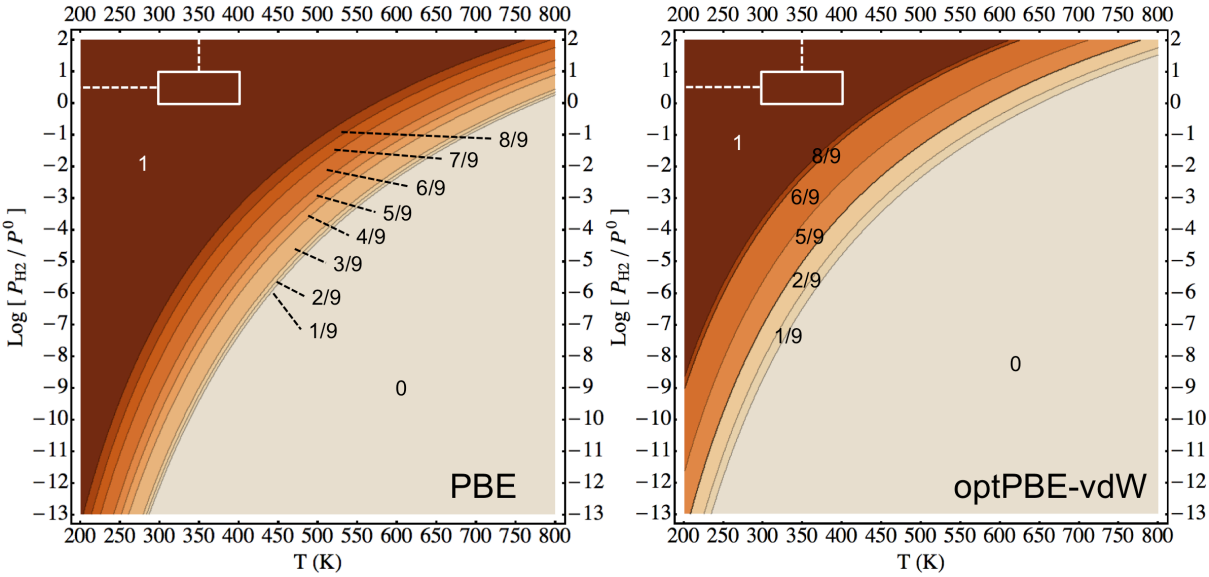


Figure 2: Surface stability diagram for H on the Pt(111) surface, indicating the optimal coverage (in ML) as a function of the pressure of H_2 and of the temperature for the PBE functional (left) and the optPBE-vdW functional (right).

The adsorption free energy of hydrogen on Pt(111) as a function of temperature (for a pressure P_{H2}=1bar) is shown on figure 1, each line on the graph corresponding to a given H coverage. The 2D surface stability diagram, indicating the optimal coverage as a function of hydrogen pressure and temperature is given in figure 2. At high temperature and low pressure, hydrogen is not stable on the surface due to the large gain of entropy in the gas phase. Upon decrease of the temperature or increase of the pressure, hydrogen will start to adsorb. Then the coverage quickly and gradually rises until a plateau corresponding to the saturation coverage of 1ML. The small size of the plateaus on the graph is linked with the small repulsion energy between H adsorbates. At typical hydrogenation reaction conditions (P= 1-10 atm, T=300-400 K), a full coverage of 1 ML is hence expected if the catalyst is exposed only to hydrogen gas. The surface free energy is calculated here by assuming that all translation degrees of freedom for H are lost when adsorbed on the Pt(111) surface, an approximation that might no be valid at low coverage, but is certainly correct at medium and high coverage, which are the situations of interest here. Easy diffusion of H on the surface and a quasi-2D gas behavior would further stabilize the low coverage situations and extend their existence domain. 2D diffusion is however quickly hindered by lateral interactions, and this should not affect the zone of the diagram close to catalytic hydrogenation conditions.

The optPBE-vdW diagram is qualitatively very similar. Two differences should be underlined. The diagram is shifted, by ~100K to lower temperature for a given pressure or by about 2 orders of magnitude to higher pressure for a given temperature. This is consistent with the fact that the adsorption energies calculated with optPBE-vdW are lower in absolute value than those calculated with PBE, which means that hydrogen sticks less to the surface. A second remark is that although the average adsorption energy per H atom monotonically decreases (in absolute value) upon coverage, the differential adsorption energy (when adding a H atom to a surface with already n H atoms) is not monotonous with

optPBE-vdW. As a consequence, some coverage values (3/9, 4/9 and 7/9 ML) are not associated with a stability domain on the surface energy diagram.

3.2- Adsorption of hydrogen on Pt_2Sn/Pt(111)

The energy profile of H on the Pt_2Sn/Pt(111) surface alloy is rather different than that on Pt(111). For both functionals, the top site on Pt is the most stable one. There is no Pt_3 hollow site on the surface alloy, and the Pt_2 bridge site is significantly less stable than the top site (by 0.17 eV for PBE and 0.21 eV for optPBE-vdW). The marked preference for the singly bonded top site contrasts with the rather flat potential energy surface on Pt(111). The adsorption of H on the Sn atom, or on a site comprising a Sn atom, is very unfavorable, so that only the Pt top sites (and bridge sites) are accessible. The presence of Sn hence separates the Pt atoms and provides well-defined Pt ensembles on the surface for adsorption with H. The separation of the surface Pt atoms by Sn has also a consequence on the electronic structure of the Pt atom. The density of states projected on the dz^2 atomic orbital, instead on being delocalized on the d band, shows a major peak at 0.5 eV below the Fermi level (see SI). Upon interaction with the H atom, this dz^2 peak is shifted to lower energy by direct overlap with H. This localized character of the dz^2 orbital of Pt in the surface alloy and its specific contribution to the bonding explains the preference for top site on Pt_2Sn/Pt(111).

In addition the adsorption energy of hydrogen is significantly weakened on Pt_2Sn/Pt(111) compared to Pt(111) (by 0.2 eV for the PBE functional and 0.18 eV for optPBE-vdW). As described before, this destabilisation of adsorption results from a small increase of electronic density on the Pt atom, which enhances the Pauli repulsion and destabilizes the adsorption.[19] The resulting surface stability diagram is given in Figure 3.

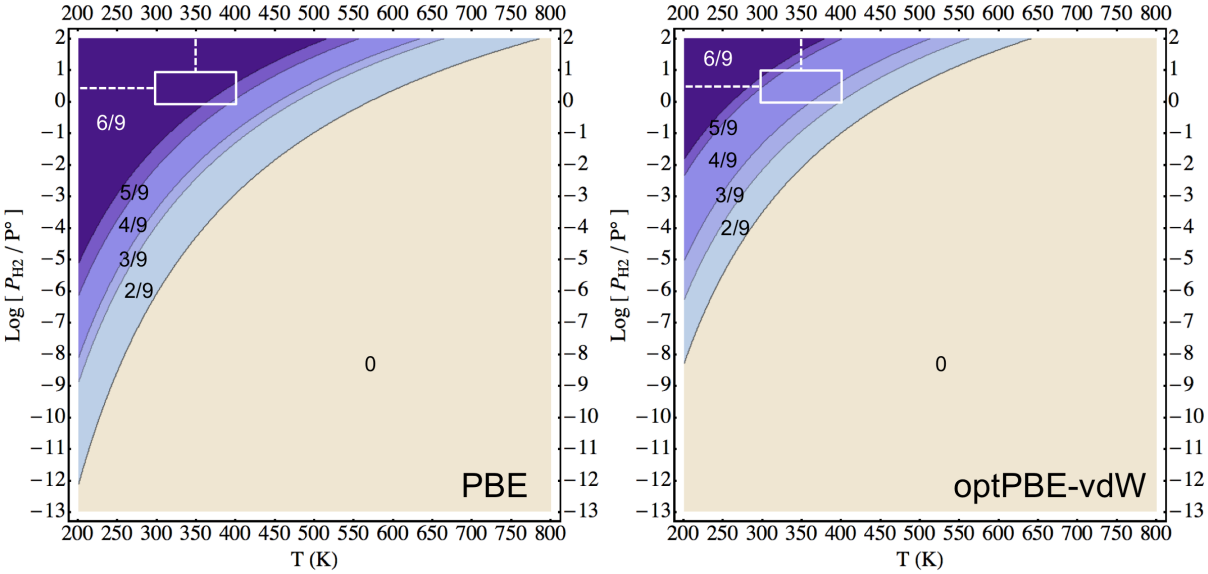
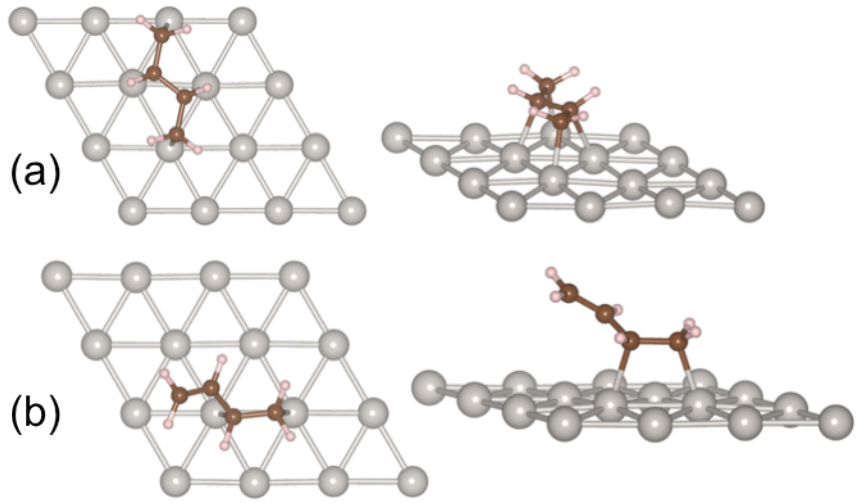


Figure 3: Surface stability diagram for hydrogen atoms on the Pt_2Sn/Pt(111) surface, indicating the optimal coverage (in ML) as a function of the pressure of H_2 and of the temperature for the PBE functional (left) and the optPBE-vdW functional (right).

The diagram has a similar shape compared to that on Pt(111) with two important differences. The saturation coverage is 2/3 ML since the Sn atoms are excluded for H and the zone boundaries are shifted to lower T and higher P values, since the adsorption energy is smaller. In the catalytic reaction conditions, the H coverage on the surface alloy is high but not completely total, with a range of 0.56-0.67 ML for PBE and of 0.33-0.67 ML for optPBE-vdW. The influence of the functional on the diagram is similar to that on the Pt(111) surface, optPBE-vdW shifting the stability zones to lower temperature (by ~150K) and to higher pressure. In this case however the H coverage value in realistic temperature and pressure conditions is affected by the choice of the functional.

3.3- Butadiene and hydrogen co-adsorption on Pt(111)

Since in realistic pressure conditions the coverage of H atoms on the catalysts is high, the butadiene will not find a bare surface to chemisorb which opens the question of the competition between hydrogen and butadiene for the adsorption sites. The low coverage adsorption of butadiene on a bare Pt surface was already studied with the PBE functional and recently with the optPBE-vdW functional.[10,11,20] Several binding mode have been found depending on the number of surface atoms involved and on their mode of coordination with the unsaturated chain. In the absence of hydrogen, the most stable adsorption mode is the trans-tetraσ configuration shown in scheme 2, with 4 σ Pt-C bonds established and an adsorption energy of -1.89 eV with PBE and -2.30 eV with optPBE-vdW (see scheme 2a). The adsorption situation involving only one double bond (di-σ mode) is less stable with an adsorption energy of -1.02 eV with PBE and of -1.49 with optPBE-vdW (scheme 2b).

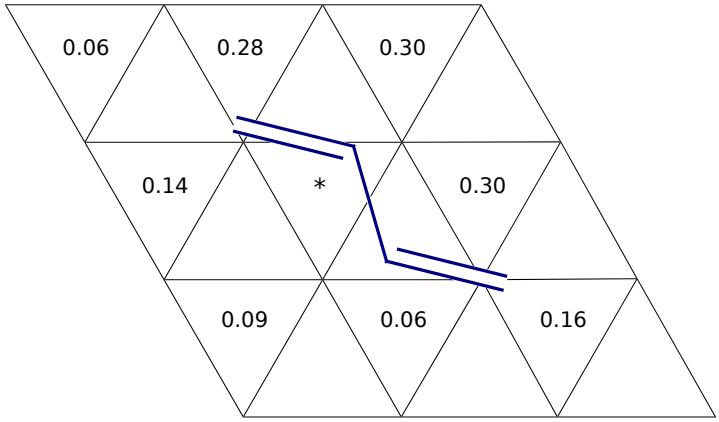


Scheme 2: Two adsorption modes of butadiene on a Pt(111) surface at low coverage: a) the most stable trans-tetraσ; b) the mestastable di-σ mode involving only one double bond.

The co-adsorption of butadiene and hydrogen was systematically studied by screening the possible configurations for 1 to 9 H atoms present in the (3×3) unit cell (H coverage from 1/9 to 8/9 ML). The screening was initially performed with the PBE functional using a 4 layer-thick slab and a more approximate (3×3×1) K-point mesh. The most stable structures were then re-optimized in our accurate conditions i.e. with a 6 layer-

slab and a dense (7×7×1) mesh. Six chemisorption structures of butadiene were used for this screening, to check if the most stable structure of butadiene was depending on the presence of co-adsorbed H atoms. It was initially assumed that the butadiene molecule is chemisorbed on the surface, to determine the optimal number of H atoms around it as a function of temperature and pressure. The detailed results of this screening procedure are given in table S1 and S2 in the SI.

The results are simple to present. Sharing a Pt atom between a carbon atom of butadiene and an adsorbed H atom results in a destabilization of the energy. The H atoms will hence prefer to occupy sites where no Pt atom is interacting with a C atom. Occupying a fcc hollow site having one Pt atom linked with a C atom destabilizes the H adsorption energy by 0.1-0.2 eV, and those with 2 such Pt atoms by 0.3 eV (see scheme 3). This through-surface repulsion between closely coadsorbed H and butadiene is complemented by a direct through-space repulsion when the H atom approaches the electron density of butadiene.



Scheme 3. Destabilizing lateral interaction (in eV) between hydrogen and butadiene for the 9 fcc hollow sites of the 3×3 Pt(111) surface using the PBE functional. * indicates a site where the adsorption of H is not stable.

At high H coverage, for a surface with a chemisorbed butadiene molecule, a compromise must be established between increasing the number of chemisorbed H atoms and occupying sites bearing large through-surface or through-space repulsion with chemisorbed butadiene. The trans-tetraσ chemisorption mode of butadiene remains the most stable one for all the values of H coverage explored, except for the high H coverage of 8/9 ML, where the di-σ form, with one double bond de-coordinated, is the most-stable mode possible for the molecule, but still presenting large lateral repulsions. The cis-1,4diσ-2,3π mode of chemisorption for butadiene is only 0.2 eV less stable and occupies three surface Pt atoms, versus four for trans-tetraσ. Upon H co-adsorption, although the energy difference is reduced to ~0.1 eV, this mode stays less stable than trans-tetraσ until a coverage of 8/9 ML, where di-σ adsorption is even more stable. Hence the cis-1,4diσ-2,3π mode is never favored by H co-adsorption (see table S2 in the SI).

If we now inverse the viewpoint and consider instead the adsorption energy of butadiene on a hydrogen pre-covered surface, the calculated results are shown in figure 4. The hydrogen atoms are supposed here to be mobile and to adopt the configuration that

optimizes the energy for the co-adsorption (butadiene adsorption energy is evaluated using that configuration as a reference). Using PBE the adsorption energy regularly decreases as a function of number of H (by 0.32 eV (17 %) for 3H and 0.72 eV (38 %) for 5 H) in agreement with the previous publication on Pd.[13] The behavior for optPBE-vdW is more stepwise, with first only a slow decrease of the adsorption energy (by 0.15 eV (7 %) for 3H and 0.46 eV (20 %) for 5H) and then a marked weakening at 6 H where a physisorbed situation is reached.

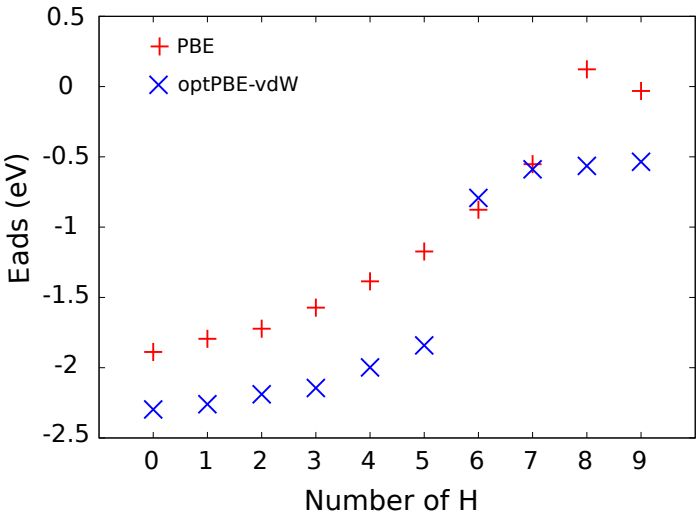


Figure 4: Adsorption energy of butadiene as a function of the number of coadsorbed H atoms on a 3×3 supercell of Pt(111). Results from the PBE (resp. optPBE-vdW) are shown with red plus (blue cross) signs.

The surface stability diagram for H on a Pt(111) surface where butadiene is constrained to be adsorbed, is shown in figure 5 for the trans-tetraσ and the di-σ chemisorption mode. The low coverage adsorption limit is only slightly modified compared to case without butadiene (figure 2). However, the repulsion with the chemisorbed molecule sets up quickly with an increased number of H atoms and the necessity to occupy more repulsive sites closer to butadiene. Hence the stability plateaus are larger than on the bare surface. In normal conditions (300K, $P(H_2)$=1 bar), and using the PBE functional, a coverage of 0.56 ML is reached for H in the presence of a tetra-σ butadiene molecule on the surface instead of 1 ML for the bare surface. This corresponds to 5 H atoms instead of 9 on the (3×3) unit cell and hence is linked with an effective occupation of 4 sites by butadiene, leaving 5 for the H atoms. The saturation coverage of 0.78 ML is only accessible at low temperature and higher pressure, beyond usual working conditions. The di-σ chemisorption mode clearly occupies less space on the surface and the plateaus remain narrow until the 4th hydrogen is adsorbed (coverage of 0.44 ML). The coverage in normal conditions reaches 0.67 ML, so that the molecule effectively occupies 3 sites.

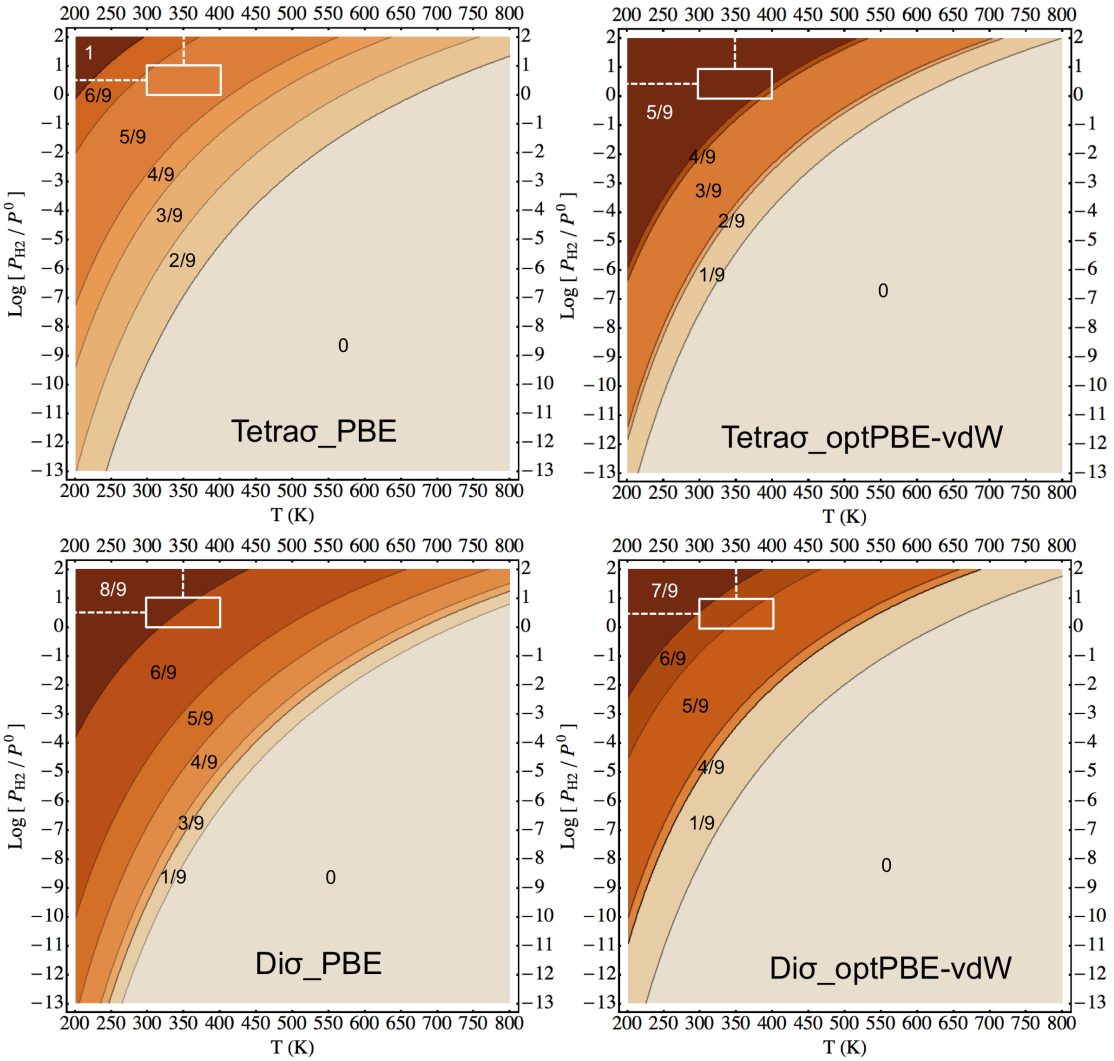


Figure 5: Surface stability diagrams for H on a Pt(111) surface where butadiene is constrained to be adsorbed in the trans-tetraσ (top) and the di-σ chemisorption mode (bottom). The left diagrams are calculated with the PBE functional, while the right ones are with optPBE-vdW.

The situation with the optPBE-vdW functional is similar, even if some intermediate coverage cases are not stable. In normal conditions, the same coverage of 0.56 ML is reached. H adsorption energy being smaller with this functional, the saturation coverage in the presence of tetra-σ butadiene is decreased to 0.56 ML, since it is not possible for H to occupy sites involving significant repulsion with the molecule.

The stability diagrams of figure 5 are constructed by imposing the chemisorption of butadiene, and hence the configuration reached is not necessarily the overall most stable one. To fix this issue, we allowed competition between configurations considering butadiene adsorbed and butadiene desorbed. This is illustrated in figure 6. On these diagrams, the chemical potential of H and that of butadiene need to be considered. We have varied the pressure of hydrogen as before (Y axis) and kept for butadiene a chemical potential equivalent to a pressure of 1 bar in a gas phase state. Note that at low

temperature, butadiene will transform in the liquid state, an effect that has not been considered here.

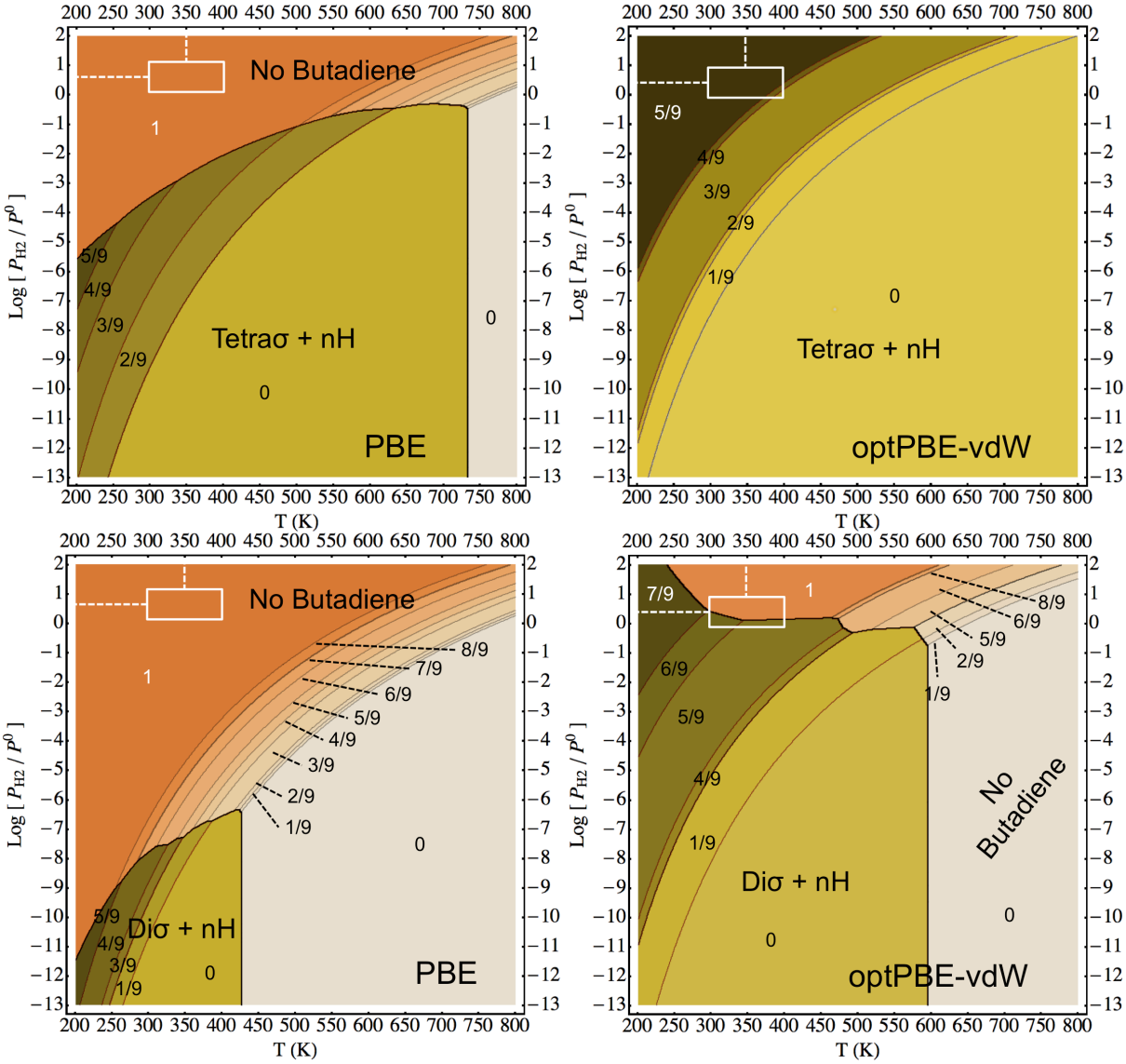


Figure 6: Overall surface stability diagram for butadiene and hydrogen co-adsorption on Pt(111), showing the most stable conformation as a function of T and P when comparing the adsorption of only hydrogen (orange zones) to the co-adsorption of hydrogen and butadiene (green/yellow zones). The top panels correspond to the most stable butadiene chemisorption mode, trans-tetraσ in any case, calculated with PBE (top left) and optPBE-vdW (top right). In the bottom, the butadiene is only allowed to adopt the less stable diσ mode, calculated with PBE (bottom left) and optPBE-vdW (bottom right). P(butadiene) is fixed to 1 bar.

The free energy of adsorption as a function of the temperature for P(H_2)=P(butadiene)=1 bar is plotted in addition on figure 7. This corresponds to a horizontal section of the diagrams of figure 6, at PH_2= 1 bar.

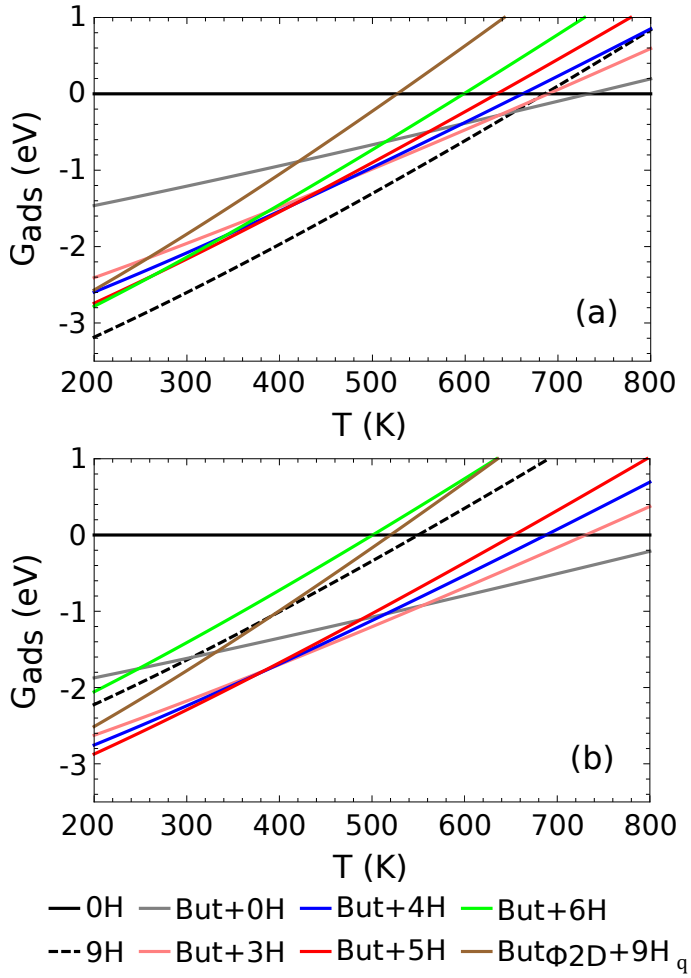


Figure 7: Free energy of adsorption calculated with PBE (a) and optPBE-vdW (b) for various butadiene-hydrogen coadsorption situations on Pt(111) as a function of temperature for $P(H_2)$=P(butadiene)=1 bar. The free energy is calculated using the 3×3 supercell.

The top diagrams of figure 6 correspond to the unconstrained situation where the overall most stable surface structure is indicated. Obviously the surface stability diagrams are different for the two considered functionals. Using optPBE-vdW, butadiene remains adsorbed all over the diagram, accommodating around it a variable amount of hydrogen atoms as a function a hydrogen partial pressure and temperature. The diagram is identical to the case of figure 5 where chemisorbed tetra-σ butadiene was imposed. For PBE however (Figure 6 top left) things are different, and butadiene remains chemisorbed only in the bottom part of the diagram where the hydrogen partial pressure is low. In the upper part, and especially for the reactions conditions, butadiene remains in the gas phase for the most stable termination that is covered only by hydrogen atoms. Hydrogen chemisorption is favored upon butadiene per surface unit area, in this pressure and temperature regime. The dominant character of hydrogen is increased if chemisorption of butadiene is only allowed in the weaker di-σ coordination mode. If we constrain the adsorption to the di-σ mode (that would be the one adopted by butene), already for optPBE-vdW, the molecule is

mostly not chemisorbed in catalytic conditions, and for PBE, butadiene chemisorption is only possible for H_2 pressure lower than $\sim 10^{-7}$ bar.

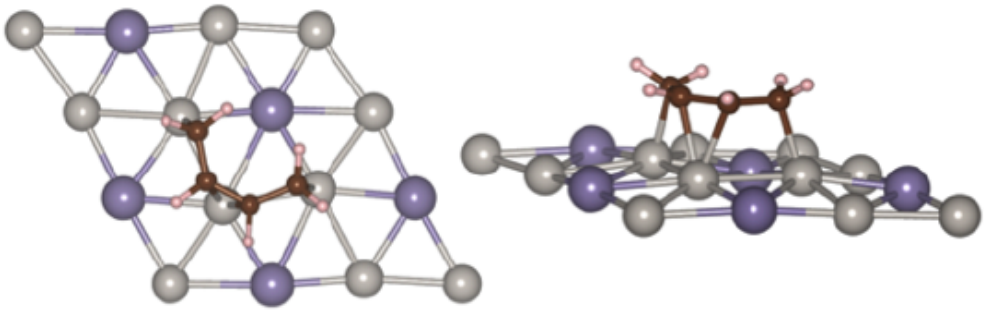
Figure 7 gives a better view of the free energy difference between the most stable state and the low-lying metastable ones. With the PBE functional (Figure 7 top) in the 300-400 K range, the one-monolayer hydrogen structure (9H on the 3×3 cell) is clearly the most stable one. Low-lying structures involving chemisorbed butadiene are at least 0.44 eV less stable at 350 K, the most stable one being associated with a H coverage of 5/9 ML (although situations with 4/9 or 6/9 ML of H are very close in energy). Starting from the hydrogen monolayer, its formation would require desorption of 4 H atoms from the cell (with a cost of 0.80 eV at 350 K) and the favorable adsorption of butadiene on this surface (gain of 0.36 eV at 350K). OptPBE-vdW provides a very different picture. As indicated before, the most stable situation in the 300-400 K range corresponds to butadiene chemisorbed in a tetra-σ mode together with ~5 H atoms on the (3×3) cell. The H monolayer structure is 0.6 eV less stable in this temperature range, and the inclusion of a physisorbed butadiene on this H monolayer only stabilizes the system by 0.14 eV.

The two functionals hence describe a very different balance between H and butadiene adsorption on the Pt(111) surface in the conditions of hydrogenation. The PBE functional favors H versus butadiene, in a way that butadiene is not adsorbed, but remains in the gas phase for the most stable configuration. This does not agree with the generally admitted Langmuir Hinshelwood scheme where both partners need to be chemisorbed for optimum reactivity. It does not agree also with the measured kinetic reaction orders for the reaction of about 1 for hydrogen and zero for butadiene, which would tend to be associated with the opposite situation of a small coverage of hydrogen, and a large coverage of butadiene. The co-adsorption situation can be reached, but only as a short-lived metastable state. Although we do not have a calorimetry measurement of the chemisorption energy of butadiene, by comparison with other unsaturated hydrocarbons (as benzene or cyclohexene) it is clear that this butadiene adsorption energy on Pt(111) is significantly underestimated (in absolute value) by the PBE functional. In contrast, the direct comparison with calorimetry shows that H adsorption energy is overestimated by PBE, by 0.15 eV for ½ H_2. This might seem acceptable, but when multiplied by the number of H atoms covering the area of butadiene (four) this comes to a more critical 0.6 eV error. As a result, opposite quantitative errors in adsorption energies of butadiene and hydrogen yield to a qualitatively incorrect description of the co-adsorption in realistic conditions.

The picture provided by optPBE-vdW is different, and agrees better with experiment. The balanced coadsorption of H and butadiene in realistic temperature and pressure conditions is in line with the admitted Langmuir Hinshelwood mechanism. The H adsorption energy is weaker by 0.1 eV than that with PBE and hence is in much better agreement with calorimetry. In contrast, the adsorption energy of unsaturated hydrocarbons is increased in absolute value (+0.4 eV for butadiene) and the error versus calorimetry data is considerably reduced for benzene for example.[20] All factors tend to concur to the conclusion that optPBE-vdW provides a much better description of the competition between hydrogen and butadiene adsorption, and yields a correct representation of the co-adsorption of these reactants in realistic conditions.

3.4- Butadiene and hydrogen co-adsorption on Pt_2Sn/Pt(111)

We can now turn to the technically interesting Pt_2Sn/Pt(111) alloy surface, since it allows the selective formation of butenes, and assess the co-adsorption of butadiene and hydrogen with our two functionals, in comparison with the case of Pt(111). The approach parallels the one taken for Pt(111) and figure 8 and 9 correspond to figure 6 and 7 previously discussed. We have already seen than hydrogen adsorption is weaker by ~0.2 eV on the alloy surface compared to Pt(111). The adsorption energy of butadiene is also considerably decreased, and this for two reasons. First, butadiene requires 4 Pt atoms in a rhombus arrangement for the most stable trans-tetra-σ adsorption. Such a surface configuration is not present on the alloy surface, and interaction with Sn is highly unfavorable. The most stable geometry is the cis-**1**,**4**diσ-**2**,**3**π, which requires only 3 Pt atoms (scheme 4).



Scheme 4: Structure of the cis-**1**,**4**diσ-**2**,**3**π chemisorption of butadiene on the Pt_2Sn/Pt(111) surface alloy. Left: top view; right: side view. Only the surface layer is shown for clarity.

This adsorption mode exists on Pt(111) and it is ~0.2 eV less stable than the trans-tetra-σ one.[10] The second aspect is that, for a given binding mode, the chemisorption of butadiene on the alloy is much weaker than that on Pt, mainly because the Pt atoms have an increased electronic density resulting from a charge transfer from Sn. The calculated adsorption energy is 0.82 eV (PBE) or 1.23 eV (optPBE-vdW), hence ~1eV lower than the best chemisorption on Pt(111).

The surface stability diagrams are shown on figure 8. The zone with butadiene adsorbed (red) are obviously reduced compared to the case of Pt(111), mostly from the fact that butadiene desorbs at a lower temperature (~350K for PBE and 500K for optPBE-vdW). Below this desorption temperature, butadiene is co-adsorbed with hydrogen with optPBE-vdW, the number of surface hydrogen being reduced by 3 compared to the hydrogen only conditions, in line with the fact that butadiene occupies 3 Pt sites on the alloy surface. In realistic conditions, butadiene is hence coadsorbed with 3 H atoms. For the PBE functional, from the weaker chemisorption of butadiene (by 0.4 eV), the co-adsorption zone is limited to low H pressure, and in realistic conditions, the surface is only (and fully) covered by 6 H atoms (per 3×3 supercell there are 6 Pt atoms) while butadiene remains in the gas phase.

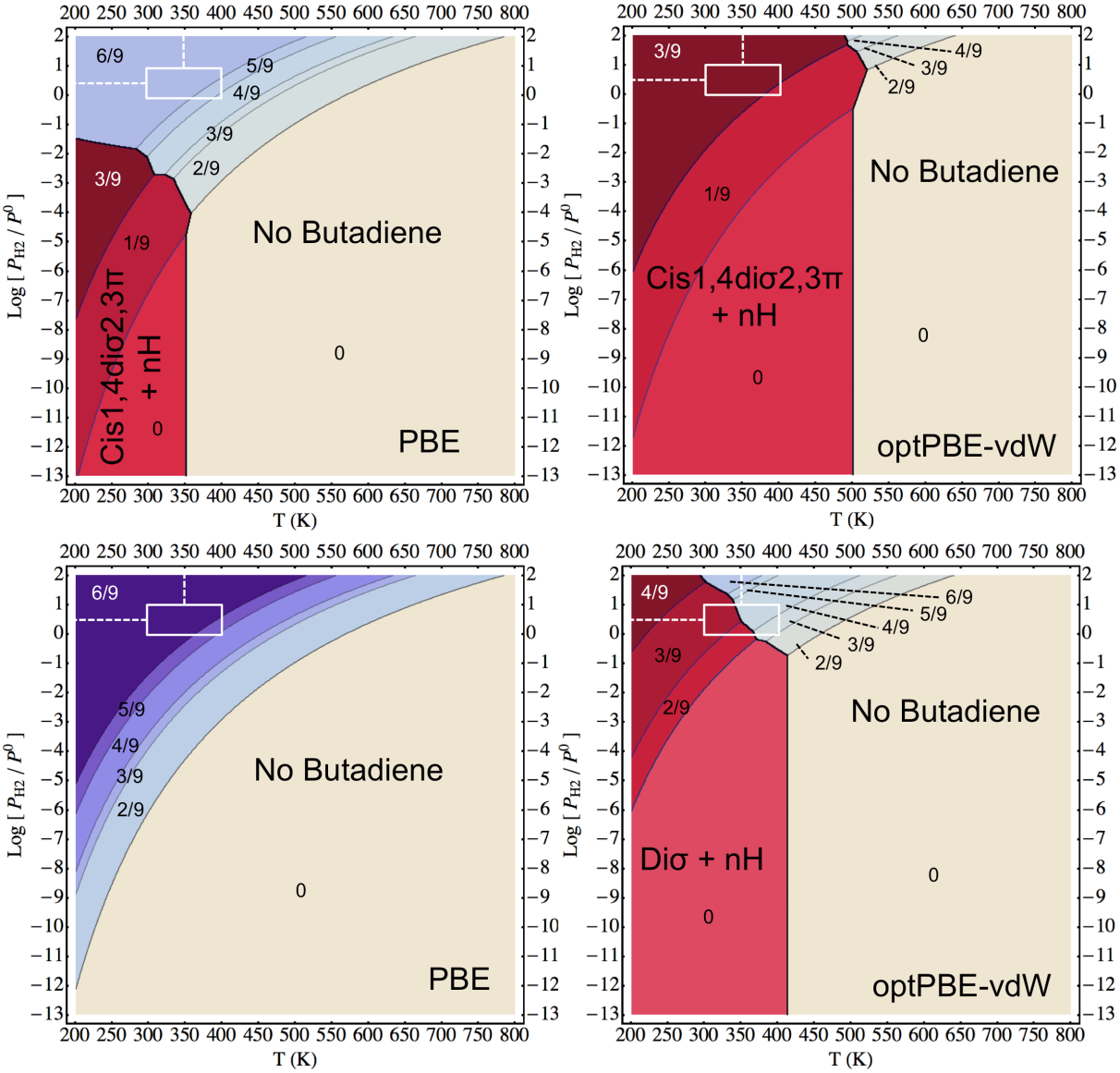


Figure 8: Surface stability diagram on the Pt_2Sn/Pt(111) surface alloy showing the most stable conformation as a function of T and P when comparing the adsorption of only hydrogen (purple) to the coadsorption of hydrogen and butadiene (red). The top panels correspond to the most stable butadiene chemisorption mode, cis-**1**,**4**diσ-**2**,**3**π in any case, calculated with PBE (top left) and optPBE-vdW (top right). In the bottom, the butadiene is only allowed to adopt the less stable diσ mode, calculated with PBE (bottom left) and optPBE-vdW (bottom right).

Similar to the case of Pt(111), the di-σ mode shows a weaker chemisorption than the tetra-σ case, although the energy difference between the two chemisorption modes is smaller (0.42 eV for PBE and 0.25 eV for optPBE-vdW). Hence for the di-σ mode the co-adsorption zone is reduced (figure 8 lower panels). This is obvious for PBE where, if butadiene chemisorption is limited to the diσ structure, coadsorption disappears completely from the diagram, giving only hydrogen adsorption. The situation is a bit more subtle for optPBE-vdW, yielding in realistic conditions a quasi equal stability for the co-

adsorbed and the H-only structures, in a way similar to the case of Pt(111). The free energy values, as a function of temperature and for a pressure p(H_2)=1 bar, are given in figure 9.

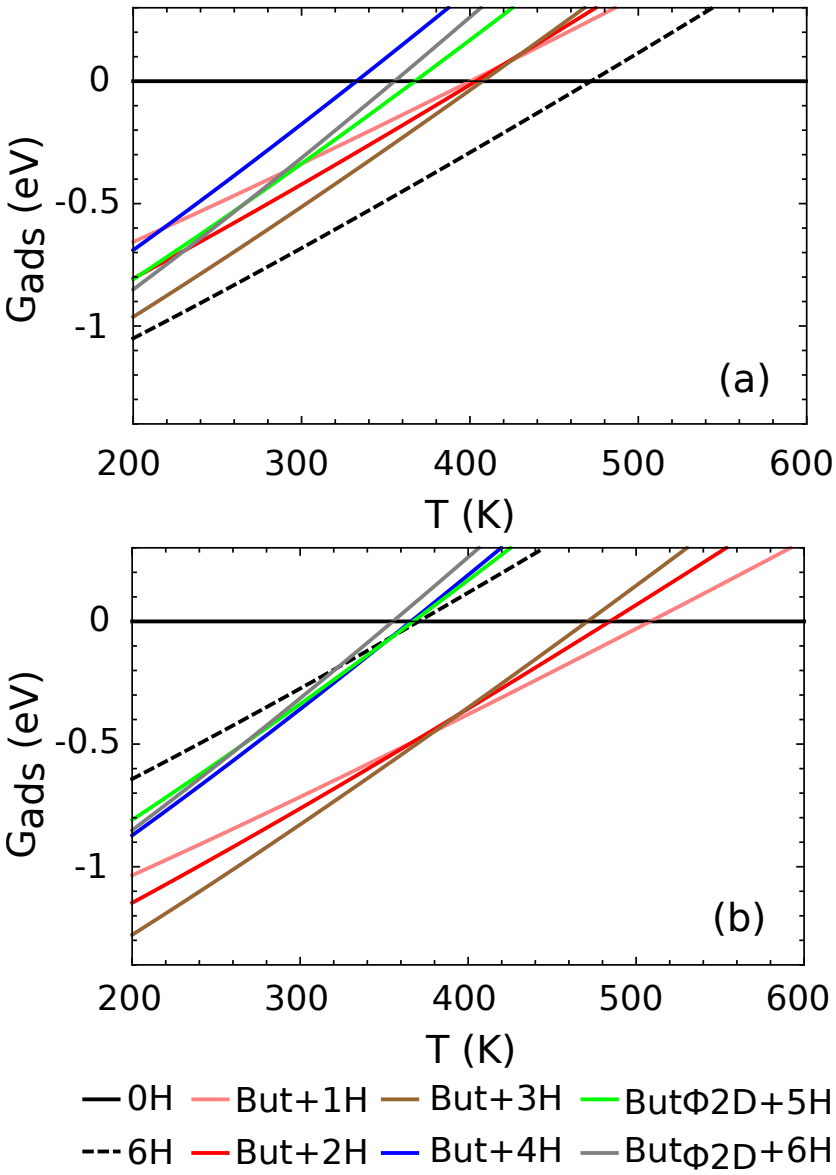


Figure 9: Free energy of adsorption calculated with PBE (a) and optPBE-vdW (b) for various butadiene-hydrogen coadsorption situations on Pt_2Sn/Pt(111) as a function of temperature for P(H_2)=P(butadiene)=1 bar. The free energy is calculated using the 3×3 supercell.

In the 300-400K interval, with PBE, the 6H (and no butadiene) chemisorption structure is clearly the most stable, and the first metastable situation, corresponding to butadiene co-adsorbed with 3H, is 0.21 eV less stable at 350 K. Starting from the most stable 6H surface, the formation of this co-adsorbed structure would require desorption of 3 H atoms from the cell, with a cost of 0.1 eV at 350 K. This is much lower than the cost required on Pt(111) since adsorption energy is weaker and only 3 instead of 4 H atoms are desorbed. However, butadiene chemisorption is also weaker and on the 3H surface is even

metastable, destabilizing by 0.1 eV. The situation is completely reversed for optPBE-vdW, with the co-adsorption situation of butadiene and 3 H atoms being more stable than the 6H structure by ~0.5 eV.

Hence, the optPBE-vdW functional also gives a picture of the coadsorption of butadiene and hydrogen on Pt_2Sn/Pt(111) which is balanced, with both species on the surface in catalytic conditions, in agreement with the admitted Langmuir-Hinshelwood mechanism, and in line with the efficient catalytic activity of this surface. In contrast, the picture for PBE is strongly dominated by hydrogen, and would require for Langmuir-Hinshelwood hydrogenation to first pay a significant energy cost to create a metastable configuration where both hydrogen and the unsaturated molecule are present on the surface.

4-Computational details

The calculations were performed within the density functional theory (DFT) framework using the Vienna Ab Initio Simulation Package (VASP) which achieves periodic calculations using periodic boundary conditions based on a plane-wave basis set.[26,27] The projector augmented wave (PAW) method is used to describe the electron-ion interaction.[28] The basis set cut off was set to 400 eV and a second-order Methfessel- Paxton smearing of 0.2 eV was used. For each system the convergence of the adsorption energy with respect to the thickness of the slab and the Monkhorst-Pack k point grid was tested to determine the most accurate and computationally efficient set up (see SI). The surface was modeled by a two-dimensional slab in a three dimensional periodic cell generated by introducing a vacuum in the direction perpendicular to the surface (width 12 Å). The two surface catalysts Pt(111) and Pt_2Sn/Pt(111) were modeled by a six-layers slab; for the surface alloy, only the uppermost layer contains tin atoms in a stoichiometry Pt_2Sn with the $(\sqrt{3}\times\sqrt{3})R30°$.structure (see scheme 1).[21,22] The geometric optimizations were carried out allowing the atoms and the uppermost two layers of the metallic surface to relax with a force criterion of 0.01 eV/ Å; the other layers were kept fixed in the bulk geometry. The Pt-Pt distance was initially optimized from Pt bulk calculations. It was found to be 2.814 Å and was used for the frozen part of the slab.

The coverage of hydrogen (θ_H) given in monolayer (ML) is defined by the ratio of the number of hydrogen atoms adsorbed on the surface and the number of atoms from the surface.

The structures were relaxed allowing hydrogen atoms to diffuse on the surface. The 2D Brillouin-zone integration was performed using a 7×7×1 (G_{ads} results) mesh for the (3×3) super-cell.

Details of the thermodynamic approach are given in the SI.

5- Conclusion

In this paper we have combined DFT and atomistic thermodynamics calculations in order to determine the most stable co-adsorption structure between butadiene and hydrogen on two surfaces: Pt(111) and the surface alloy Pt_2Sn/Pt(111). Reaction conditions have been changed in a large interval of temperature and hydrogen partial pressure, while the partial pressure of butadiene was maintained at 1 bar. The discussion was centered on conditions typical for hydrogenation reactions with a temperature between 300 and 400 K and a hydrogen pressure ranging from 1 to 10 bar. Two DFT exchange-correlation

functionals have been used and compared: PBE, a standard semi-local one, and a more recent non-local functional, optPBE-vdW.

The main qualitative conclusion, surprising at least to us, is that the two functionals give a strongly contrasting answer, resulting from a different balance between butadiene and hydrogen adsorption strengths. At typical hydrogenation conditions, PBE gives as most stable situation a surface fully covered with hydrogen, corresponding to 1 hydrogen atom per surface Pt atom on both surfaces (on a 3×3 unit cell there are 9 Pt atoms for Pt(111), and 6 Pt atoms for Pt_2Sn/Pt(111)). At 350 K, the most stable co-adsorbed situation, comprising one butadiene and five (resp. three) H atoms for a (3×3) cell of Pt(111) (resp. Pt_2Sn/Pt(111)), is less stable by 0.44 eV (resp. 0.2 eV). This result does not agree with the experimental data for butadiene hydrogenation kinetics on Pt(111), both in terms of activity and of reaction orders (the order is around zero for butadiene and 1 for hydrogen). It could be envisaged that the fully hydrogen covered Pt(111) surface could be first transformed into a reactive state by desorbing 4 hydrogen atoms, hence creating a depleted area on which butadiene could adsorb and react. The energy required for the creation of such a "hole" at hydrogenation conditions (0.80 eV) is however too high to reach an efficient hydrogenation activity. On the surface alloy model, the results are qualitatively similar, but the creation of the "hole" requires desorption of only 3 hydrogen atoms (because the butadiene adsorption mode is different) and is not as energy demanding, since hydrogen adsorption is weaker on the alloy.

The optPBE-vdW functional provides opposite results, giving a co-adsorption of butadiene and hydrogen as the most stable situation. On the (3×3) cell of Pt(111) (resp. Pt_2Sn/Pt111) butadiene is accompanied by five (resp. three) H atoms. If only hydrogen is adsorbed, nine (resp. six) atoms are positioned on the (3×3) cell for Pt(111) (resp. Pt_2Sn/Pt(111)), but this situation is now 0.6 eV (resp. 0.5 eV) less stable that the co-adsorbed case at 350 K. The H-only and Butadiene-H coadsorbed structures hence correspond to the same optimal H coverage for the two functionals, but their relative energies strongly differ (by 1.04 eV for Pt(111) and 0.7 eV for Pt_2Sn/Pt(111). The most stable co-adsorbed situation obtained for the optPBE-vdW functional naturally provides configurations favorable for butadiene hydrogenation following the Langmuir-Hinshelwood mechanism.

The different description of competitive adsorption between hydrogen and butadiene from the two functionals has two origins. First the adsorption of butadiene is markedly stronger with the optPBE-vdW functional (by 0.4 eV), because this functional describes much better the weak dispersion interactions with its non-local correlation kernel.[24] Although the molecule is strongly (covalently) chemisorbed on the two considered surfaces, the contribution of non-bonded interactions between molecule and second neighbor Pt atoms is large.[20] A second effect comes from the hydrogen atom, which adsorption is slightly weaker with optPBE-vdW from a different exchange functional. The effect per H atom is only 0.1 eV, but since the two compared structures differ by 4 (or 3 hydrogen) atoms this provides the second part of the observed energy difference. A benchmark against adsorption energies measured by single crystal micro-calorimetry shows that optPBE-vdW is more accurate than PBE for the chemisorption of unsaturated hydrocarbon molecules and of hydrogen on Pt(111).[20,29] It is hence natural that this functional gives a better balance between butadiene and hydrogen adsorption and provides a co-adsorption situation in line with experiments. It can hence be recommended for

studies dealing with unsaturated hydrocarbon and hydrogen. Only two functionals have been tested here, and besides optPBE-vdW, other functionals could also reach a correct balance. It is clear however that the description of dispersion interactions is required to obtain an accurate value of the chemisorption energy of the unsaturated hydrocarbon and a good description of the hydrogen-butadiene co-adsorption on Pt(111).[20]

The computational study of co-adsorption systems from DFT can hence be delicate. Indeed, errors do not only impact the quantitative adsorption energy of one adsorbate, but they might cumulate over several and finally provide a qualitatively wrong picture of the optimal co-adsorption situation, and large errors in the relative energies of configurations. In addition, a good performance of a DFT functional on a few systems does not guaranty accuracy on a whole class of problems. It is hence important to amplify the effort in experimental determination of adsorption energies, in order to enable a larger benchmark of DFT functionals for co-adsorption and catalytic applications.

The co-adsorption study presented here is the necessary initial step for mechanistic studies and reaction pathway searches. Temperature and pressure affects the coverage of unsaturated hydrocarbon and hydrogen, and the energy required to de-coordinate one double bond of butadiene from the surface. This can open reaction pathways and have a major importance on the kinetics of hydrogenation.

Supporting Information available

Projected density of states for Pt_2Sn/Pt(111) and H on Pt_2Sn/Pt(111). Screening procedure for the co-adsorption structures of butadiene and hydrogen. Convergence of the adsorption energy with k point grid. Description of the thermodynamic approach.

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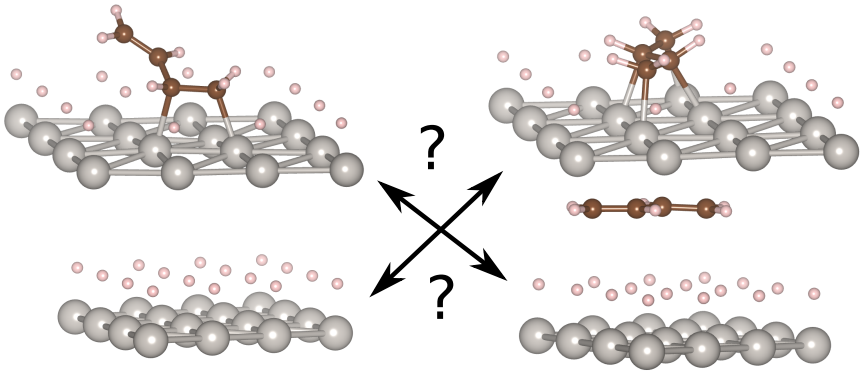
Calculations were performed using the local HPC resources of PSMN at ENS-Lyon.

TOC Graphic



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