Switch in relative stability between *cis* and *trans* 2-butene on Pt(111) as a function of experimental conditions: A DFT study

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Abstract

The adsorption of *cis* and *trans* 2-butenes on Pt(111) has been studied as a function of hydrogen coverage θ_H by means of calculations based on density functional theory (DFT) with the inclusion of dispersion forces. All hydrogen coverages have been considered, from $\theta_H = 0$ to 1.00 monolayer (ML). For each case, the di-σ and π adsorption geometries of the olefins have been compared at a surface coverage of $\theta_{C4H8} = 0.11$ ML. Calculations of the Gibbs free energies of these systems have identified the most stable 2-butene isomer (*cis* or *trans*) as a function of coverage, temperature and pressure. In particular, focus was placed on two sets of conditions, namely, one with a pressure of 10^{-7} Torr, a temperature of T = 80 K, and a gas ratio of $P_{H2}/P_{butene} = 25$, similar to the conditions used in surface-science studies, and a second with a pressure of 1 bar, a temperature range of 300-400 K, and a gas ratio of $P_{H2}/P_{butene} = 10$, similar to catalytic hydrogenation conditions. With all selected functionals (PW91, PBE-TS, optPBE), the di-σ bonding was found to be the most stable for both isomers of 2-butene and for all hydrogen coverages except for $\theta_H = 1.00$ ML. At low pressure, 2-butene is physisorbed at low temperature (up to 125K with PBE-TS and to 90K with optPBE), but when the temperature increases, the coadsorption with 6 H becomes the most stable ($\theta_H = 0.67$ ML) and finally, 2-butene desorbs around 380K (325K) with PBE-TS (optPBE).

Interestingly, a switch in stability was observed with hydrogen coverage, from the adsorbed *trans* isomer being the more stable for $\theta_H < 0.44$ ML to the adsorbed *cis* isomer becoming the more stable at higher hydrogen coverages, in agreement with the *cis-trans* isomerization behavior previously reported for this system. At high pressure, the behavior is similar but with transitions occurring at higher temperatures. 2-butene is physisorbed until 250K and desorbs beyond 500K. At hydrogenation reaction temperatures (between 300 and 500K), a coverage of roughly half a monolayer was found (0.66 and 0.44 for 300K and 500K, respectively). Our results confirm that dispersion effects must be included to properly describe the 2-butene and hydrogen coadsorption on Pt(111), as PW91 predict that 2-butene is never adsorbed on the platinum. On the other hand, DFT calculations including dispersion forces such as PBE-TS or optPBE allow a good understanding of a catalytic system, in both ultra-high vacuum conditions and under catalytic hydrogenation conditions. For this system, the PBE-TS results are in good agreement with experiments: they correctly reproduce the coverage in hydrogen and the configuration of the 2-butene adsorbate (*cis-trans* isomer).

Keywords *cis-trans* isomerization, 2-butene, Pt(111), adsorption, H coverage, free energy, temperature diagram, DFT

Introduction

Mechanistic studies in heterogeneous catalysis are often difficult because there is only a limited set of spectroscopic techniques available for the identification of surface intermediates in situ under the atmospheric pressures required for such processes.[1,2,3,4] Much more detail can be obtained by using modern surface-science approaches, but that requires the use of ultrahigh vacuum conditions.[5,6,7,8,9] Bridging this so-called pressure gap has been a challenge. [10,11,12,13] Recently, advances in quantum mechanics calculations have provided an alternative way to establish the relative stability of different potential competing intermediates, and even to estimate activation barriers for surface chemical conversions.[14,15] However, while the influence of temperature and pressure has been taken into account in calculation of free energies in recent reports, the effect of coadsorbates has been omitted in most DFT theoretical studies reported to date. The work reported here aims to address such issue.

In the case of the adsorption and hydrogenation of alkenes, butene and butadiene in particular, the coverage of hydrogen atoms is critical, yet it has been rarely taken into account in theoretical studies.[16,17] There have been a few important reports on this effect, however: H coadsorption was explicitly taken into account for a few (typically 3) coverages in the theoretical studies of the adsorption of ethylene on Pd(110),[18] for the reactivity of ethylene[19] and acetylene on Pt(111),[20] and quite recently for the adsorption of cinchonine and cinchonidine chiral modifiers on Pt(111).[21] Monte Carlo kinetic simulations have included some of the parameters describing the experimental conditions as well, but these calculations focus on reaction kinetics and do not provide many details on the structure of the catalysts or the adsorbates.[22,23]

A better understanding at the atomistic level has been reached by combining the effect of the adsorbate coverage with the effect of temperature and pressure. In their seminal theoretical work, Chizallet *et al.* considered the effect of H_2 pressure on the stability of butadiene and 1-butene on palladium (111) and (100) surfaces, with a focus on the selective partial hydrogenation of the diene versus surface structure.[24] Recently, the group of M.-F. Reyniers studied the adsorption and hydrogenation of benzene on Pd(111) using DFT thermodynamic stability diagrams in the presence of coadsorbed hydrogen,[25] with a hydrogen coverage of 0.44 monolayers (ML), a value close to those used industrially.[26] Ferguson *et al.* constructed the phase diagram of hydrogen-guaiacol coadsorption on Pt(111) to explain the differences seen in the experimental behavior of that system as a function of the temperature and pressure.[27] Gautier *et al.* also constructed a phase diagram for 1,3-butadiene on Pt and Pt_2Sn.[28] Zhao *et al.* considered hydrogen coverage within the facet dependence of the hydrogenation catalysis of olefins on Pd(111).[29] Wang *et al.* included in a kinetic model the combined effects of hydrogen coverage, temperature, and pressure on the activity and the selectivity of the hydrogenation of furfural on Pd(111).[30] In all those recent studies, inclusion of the dispersion effects in the computation of adsorption energies proved to be essential to reproduce experimental data.[27,28,29,30,31] Such studies have been quite enlightening and have tested the boundaries of what is possible with DFT calculations to approach the description of realistic catalytic systems.

Our work is in line with those recent studies, and aims to give a clear description of the catalytic surface under realistic conditions. We focus herein on 2-butene, particularly on its *cis*-*trans* isomerization with hydrogen on platinum surfaces. Our emphasis is on the role of coadsorbed hydrogen and on the correct theoretical description of the substrate/metal interactions with DFT. The chemistry of alkenes is central to many industrial applications, and has therefore been studied in great detail already.[32] However, a number of key mechanistic queries remain still unanswered.[10,33] In particular, there are important pending questions related to the regio- and stereo-selectivity of the hydrogenation and dehydrogenation surface steps that define product selectivity in alkene isomerization processes. This stereochemistry issue is of particular importance in the food industry, as the partial hydrogenation of edible oils is often accompanied by the undesirable production of *trans* fatty acids, which are more stable than the *cis* isomers but have adverse health effects.[34] It has not been possible yet to develop catalysts to carry out partial hydrogenation of edible oils while retaining the *cis* conformation of the remaining carbon-carbon double bonds.

In connection with this challenge, results from our recent surface-science experiments using single-crystal surfaces and ultrahigh vacuum (UHV) environments have shown that *trans* 2-butene isomerizes preferentially to produce *cis* 2-butene on Pt(111) surfaces predosed with H_2.[35,36] Moreover, it was proven that the selectivity of the isomerization can be tuned under more realistic conditions by controlling the shape of the Pt particles used in supported catalysts.[37,38,39] It was shown that the isomerization of the *trans* isomer to its *cis* counterpart occurs on the (111) facets of platinum particles with tetrahedral shapes, and that the selectivity is reversed on the more open surfaces seen in more rounded nanoparticles. From temperature-programmed desorption (TPD) experiments, it was learned that *cis* 2-butene is more tightly bound to Pt(111) surfaces predosed with hydrogen (or deuterium) than *trans* 2-butene by 1.8 kcal/mol (0.08 eV).[35]

We have also reported some initial studies on the adsorption of the 2-butene isomers on Pt(111) by density functional theory (DFT) calculations in the past.[17,37,40] It was established that the preference for *trans* to *cis* isomerization may be explained by a reversal in the adsorption stability induced by coadsorbed hydrogen atoms because adsorption of the *trans* isomer requires a larger molecular deformation than the *cis* isomer on a saturated surface. However, those studies did not consider all the possible coadsorbed structures for a given set of coverages, neither did they include any dependence of the energetics on the temperature and H_2 pressures used in the catalytic reactions. The present work addresses those past shortcomings, and establishes a more realistic thermodynamic diagram showing the evolution of the stability of the whole 2-butene-hydrogen-Pt(111) system for a large range of temperatures and reactant pressures as a function of H coverage.

This report is organized as follows. First, the adsorption modes of *cis* and *trans* 2-butene on the Pt(111) surface as a function of H coverage are revisited. Then the free energies are calculated, and finally, thermodynamic diagrams are derived.

Computational details

The calculations reported here were based on the density functional theory (DFT) under periodic boundary conditions, and were performed using the Vienna ab initio simulation program (VASP).[41,42,43] The electron-ion interactions were described by the projector augmented wave (PAW) potential,[44] and the valence electrons were treated explicitly with a plane-wave basis set at a cutoff energy of 400 eV. The Pt(111) surface was modeled with a periodic slab composed of five Pt layers and a vacuum of six equivalent layers (13.8 Å) in the perpendicular direction. Adsorption was only considered on one side of the slab. During all the geometry optimizations, the uppermost Pt layers and the adsorbates were relaxed, while the two lowest layers were frozen in the optimal bulk geometry with a Pt-Pt interatomic distance of 2.82 Å. A Monkhorst-Pack mesh of 5 × 5 × 1 K points was used for the 2D Brillouin zone integration.[45] Previous studies have shown that relative adsorption energies converge within 5 meV with those settings, while absolute adsorption energies converge within 35 meV.[46,26] A (3 × 3) Pt(111) unit cell with one butene molecule (corresponding to a butene surface coverage of θ_{C4H8} = 0.11 ML; 1 ML = 1 monolayer = 1 molecule per platinum surface atom) and between 1 and 9 hydrogen atoms (θ_H = 0.11, 0.22, 0.33, 0.44, 0.56, 0.67, 0.78, 0.89, and 1.00 ML, respectively) on the surface was used throughout the study. This coverage for 2-butene is representative of what has been reported experimentally; a coverage of 0.13 ML has been estimated for *cis*-2-butene on Pt(111).[47] The molecules in gas phase were calculated at the Γ point of the Brillouin zone in a cubic box of dimensions 15×15×15 $Å^3$. A dipole correction was added for the most stable adsorption structures.

The dispersion interactions are of great importance for calculating adsorption energies of unsaturated molecules on metallic surfaces,[25,26,27,28,29,31] and were therefore included in our calculations. In the last few years, new methods and functionals have appeared for taking dispersion interactions into account. Recent reviews give a general survey of this issue.[29,48] In our previous studies, we tested some of them (namely optPBE,[49] optB86b,[49] optB88,[49] BEEF[50] and PBE-TS (Tkatchenko/Scheffler)[51]) to describe the *cis*/*trans* isomerization of 2-butene[46] and the adsorption energies of several unsaturated molecules.[29] For the adsorption of hydrogen, these tests showed that the on-top site is more stable than the fcc hollow site if the first four functionals are used, in disagreement with the experimental data,[52, 53,54] while the experimental order is respected with PW91. Concerning 2-butene, the adsorption energy is greatly increased compared to pure GGA (PW91 or PBE), by 0.6 to 0.9 eV, except for BEEF (0.1 eV), in agreement with the general statement that alkenes are too weakly bound when pure DFT is used. We thus decided to test the pure GGA function PW91[55] together with optPBE and PBE-TS because these two functionals performed well in our tests, and were also used successfully to describe the adsorption of unsaturated molecule on metallic surfaces.[25,26,27,28,29,48,56]

For each coverage of hydrogen atoms adsorbed on the Pt(111) surface, many permutations of sites are possible. As the 2-butene molecule modifies the usual relative stability of those sites, the simplest configuration where all possible fcc sites are occupied proved to be energetically unfavorable when compared with other alternatives mixing fcc, hcp, top and even bridge sites. Many configurations were manually considered for all coverages to identify the most stable structures.[57] This explorative process was conducted for the three selected density functionals, ensuring that the most stable configurations were identified for all three functionals. Additionally, *ab initio* molecular dynamics (AIMD) simulations were carried out with 7 and 9 hydrogen atoms coadsorbed with the *cis* or *trans* 2-butene to provide an unbiased sampling of the configuration space of the H atoms on the Pt(111) surface. For each 2-butene isomer, two simulations were performed: one where all hydrogen atoms were initially placed on top sites, and another where they were placed in their most stable position. Based on previous study of this system,[46] a four-layer slab and a 3 × 3 × 1 K-point mesh were chosen for these AIMD simulations with the PW91 functional. The time step was set to 0.5 fs, and the temperature was controlled using a Nosé thermostat with a coupling frequency of 420 cm^{-1} (SMASS=0.26), which corresponds to the Pt-H stretching.[58] The system was heated to up to 600 K in 2000 steps, and then propagated for an additional 10 ps. From these simulations, 10 frames were extracted and optimized. All of them converged to structures already found with our first exploration.

The energy of 2-butene with n H atoms on Pt(111) was calculated using either one of two approaches: in the first, the coadsorption energy referred to the clean surface was estimated by using Equation (1):

$$\Delta E_{\mathrm{coads}}(\mathrm{nH+But}) = E_{\mathrm{Tot}} - E_{\mathrm{But(g)}} - \mathrm{n}/2E_{\mathrm{H2(g)}} - E_{\mathrm{Pt}} \qquad (1),$$

where $E_{\mathrm{But(g)}}$ is the energy of the corresponding isomer in gas phase, and E_{Pt} the energy of the surface slab. A second way was also employed considering the adsorption energy of 2-butene on a Pt(111) surface pre-covered with n hydrogen atoms following equation (2):

$$\Delta E_{\mathrm{ads}}(\mathrm{But}) = E_{\mathrm{Tot}} - E_{\mathrm{But(g)}} - E_{\mathrm{nH@Pt}} \qquad (2),$$

where $E_{nH@Pt}$ is the energy of the Pt slab with n adsorbed hydrogen atoms.

The thermodynamic diagrams related to the Gibbs free adsorption energy have been plotted following Equations 3 to 6:[59]

$$\Delta G_{ads} = G_{ads} - G_{surf} - G_{gas} \tag{3}$$

$$G = PV - Nk_B T - NK_B T \ln\left(\frac{Q}{N}\right) \tag{4}$$

$$\Delta G_{ads}(T,P) = \Delta E_{ads} + \Delta E_{ZPE} + F_{config,ads} - NK_B T \ln\left(\frac{Q_{ads}^{vib}(T)}{Q_{gas}^{vib}(T) Q_{gas}^{rot}(T) Q_{gas}^{trans}(T)}\right) \tag{5}$$

$$F_{config,ads} = -k_B T \ln Q_{config,ads} = -k_B T \ln\left(\frac{N_{site}!}{(N_{site} - N_{ads})!\, N_{ads}!}\right) \tag{6}$$

where ΔE_{ads} and ΔE_{ZPE} are the DFT adsorption energy and the DFT zero-point energy change due to adsorption, respectively, and $F_{config,ads}$ is the configurational free energy of the adsorbed phase. Q_{ads}^{vib} and Q_{gas}^{vib} are the respective vibrational partition functions of the adsorbed system and the gas phase, computed within the harmonic oscillator approximation. Q_{gas}^{trans} and Q_{gas}^{rot} are the translational and rotational partition functions of the gas, calculated within the rigid rotor harmonic oscillator approximation :

$$Q_X^{vib}(T) = \sum_{i=1}^{3N-6} \left(1 - \exp\left(-\frac{hv_i}{\mathrm{k_B} T}\right)\right)^{-1}$$

$$Q_X^{trans}(T) = V\left(\frac{2\pi M \times \mathrm{k_B} T}{h^2}\right)^{3/2} = \frac{k_B T}{P}\left(\frac{2\pi M \times \mathrm{k_B} T}{h^2}\right)^{3/2}$$

$$Q_X^{rot}(T) = \frac{\sqrt{\pi}}{2}\left(\frac{8\pi^2 k_B T}{h^2}\right)^{3/2} I_a I_b I_c$$

Except for the diatomic H_2:

$$Q_{H_2}^{rot}(T) = \frac{1}{2}\left(\frac{8\pi^2 k_B T}{h^2}\right) I_{H_2}$$

Where h is the Planck constant and $\mathrm{k_B}$ is the Boltzman constant.

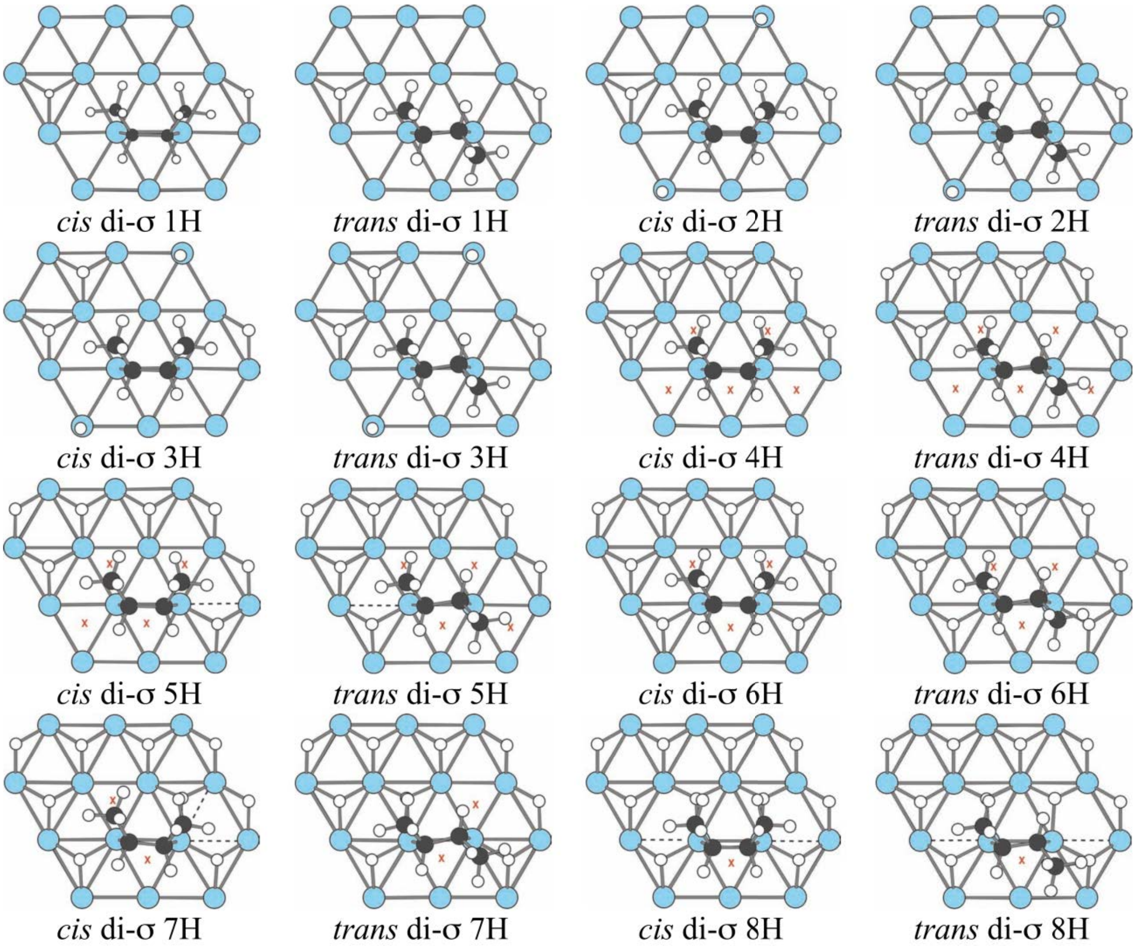
Vibrations were included in the Gibbs free energy for all systems, in line with Ferguson *et al.* observation that this is of uttermost importance.[27] Frequencies were estimated for all systems via numerical calculation of the second derivatives of the potential energy surface within the harmonic approach. The coupling between the molecular vibrations and the surface metallic phonons was taken into account. The force constant matrix (or Hessian matrix) was built with finite differences of the first derivatives of the total energy by geometrical perturbations of the optimized Cartesian coordinates of the system (0.02Å at the harmonic level). The diagonalization of this matrix provided the harmonic frequencies and the associated harmonic normal vibration modes. Typical simulations were performed between 50 and 400 K and with a P_{H2}/P_{butene} pressure ratio between 10 and 25. For each hydrogen coverage, the most stable coadsorption structure of each 2-butene conformer (*cis* or *trans*) was retained for the calculation of the Gibbs free adsorption energies; the effect of other less stable structures was incorporated within the configurational free energy $F_{config,ads}$.

Results and Discussion

Two adsorption modes are usually found for alkenes on metal surfaces, a di-σ bonding where both carbons in the double bond rehybridize to form new bonds with two different metal atoms, and a π configuration where the double bond interacts with one single metal atom via its π electrons.[60,61] On clean Pt(111) the former is usually preferred, and that is the case with 2-butene as well.[62,63] It is also known that the preferred adsorption sites for hydrogen atoms on Pt(111) are the fcc three-fold hollow sites,[52,53,54] even though the presence of 2-butene on the surface is likely to modify this preference, possibly making other positions more favorable.

In our previous work, we have thoroughly characterized the adsorption of *cis* and *trans* 2-butene on the Pt(111) surface, clean and with hydrogen coverages of $\theta_H = 0.11$ and 1.00 ML, with the PW91 functional.[46] In the case of one single H atom ($\theta_H = 0.11$ ML) coadsorbed with 2-butene on the (3×3) lattice of Pt(111), 27 positions were compared, including 9 fcc and 9 hcp three-fold hollow sites, and 9 on-top positions (for the numbering of these sites, see Figure S1, Supporting Information). The relative coadsorption energies calculated in that study and those calculated in the present work with the two other functionals are collected in Tables S1, S4 and S5, and the most stable systems are depicted in Figures S2, S8 and S10 for the PW91, PBE-TS and optPBE functionals, respectively (Supporting Information). The most stable systems for both di-σ and π geometries are summarized in Figures S3 and S4 in the case of nine H atoms ($\theta_H = 1.00$ ML) coadsorbed with the 2-butene isomers. To these results, calculations of 2-butene physisorbed on top of the Pt(111) surface covered with 1 ML of hydrogen were added. In agreement with previous experimental[64] and theoretical studies,[25,27,30,46] these systems are more stable than those corresponding to adsorbed 2-butene for all three functionals.

Starting from those results, further calculations were carried out in this study for other hydrogen coverages. A large number of configurations were tested: the resulting relative energies are collected in Tables S2 and S3, and the structures are shown in Figures S2 to S6 (all provided in the Supporting Information). In the case of surfaces covered with eight H atoms, (θ_H = 0.89 ML), both PW91 and PBE-TS favor coadsorption with 2-butene, contrary to the situation with nine H atoms. Both the adsorption, ΔE_{ads}(But), and coadsorption, ΔE_{coads}(nH+But), energies, as defined in Equations 1 and 2 respectively, are given in Table S7 (Supporting Information) for the four best structures with 2-butene plus n H atoms. The structures of the most stable form of each isomer at a given H pre-coverage, which is the di-σ geometry for hydrogen coverages of up to 8 H, are depicted in Figure 1 for PW91. The PBE-TS and optPBE most stable configurations are shown in Figures S7, S8 and S9, S10, respectively.


cis di-σ 1H *trans* di-σ 1H *cis* di-σ 2H *trans* di-σ 2H

cis di-σ 3H *trans* di-σ 3H *cis* di-σ 4H *trans* di-σ 4H

cis di-σ 5H *trans* di-σ 5H *cis* di-σ 6H *trans* di-σ 6H

cis di-σ 7H *trans* di-σ 7H *cis* di-σ 8H *trans* di-σ 8H

Figure 1: Most stable structures of the *cis* and *trans* isomers of 2-butene coadsorbed with n H atoms, n = 1 to 8 with the PW91 functional. From n= 4, the red cross(es) indicate(s) the vacant site(s). Coadsorption of 9H and 2-butene leads to physisorbed systems not represented here.

From those structures and adsorption energies, we constructed thermodynamic stability diagrams as a function of temperature and pressure. Those diagrams are meant to help fulfill the main focus of this work, which was to establish a thermodynamic criteria to evaluate the evolution of the system composed of 2-butene and n H atoms adsorbed on Pt(111) as a function of temperature and pressure. Two families of thermodynamic states were considered: the coadsorption of n H atoms and 2-butene on the Pt(111) surface, and desorbed 2-butene in gas phase with a hydrogen covered (Hn@Pt) surface. In all cases, the Gibbs free energies were calculated following Equation (5).

The accuracy of the three selected functionals to describe the adsorption energy of 2-butene on the bare Pt(111) surface (n=0) has already been discussed.[29] While there is no recent accurate experimental value, it is safe to assume that the adsorption energy of 2-butene should not differ greatly from that of cyclohexene, for which a value of 1.27 eV has been reported.[65] It was found that the pure GGA PW91 functional underestimates that energy (E_{ads}=0.95 eV), whereas PBE+TS overestimates it (E_{ads}=1.77 eV). The optPBE functional provides the best estimate at 1.53 eV. It is worth noting that the good performance of optPBE is not due to the fact that it is based on the revPBE functional and not the PBE one: revPBE predicts a very low adsorption energy of 0.44 eV (see Table S6 in Supporting Information).

Before considering the *cis*/*trans* relative stability of the olefin, we focused on the thermodynamic domains in which the 2-butene is (co-)adsorbed on the platinum surface. The diagrams obtained with P_{H2}/P_{but}=25 are shown in Figure 2. PW91 predicts that 2-butene is never adsorbed on the platinum substrate regardless of the values of temperature and pressure considered. This behavior has already been noticed before,[25,28,29] and comes from the fact that pure GGAs underestimate the 2-butene adsorption energy while overestimating the hydrogen energy (E_{ads}(PW91)=0.49 V instead of 0.38 V).[66] On the other hand, both optPBE and PBE-TS predict a large domain (shown in green and orange) in which 2-butene is coadsorbed with H atoms on the platinum surface. As a consequence, the PW91 functional will not be considered any further.

Two regimes are usually considered for studying catalytic systems on surfaces:[10] an ultrahigh vacuum regime corresponding to a pressure below 10^{-6} Torr, required for the operation of most modern surface-science spectroscopies, and a high pressure range, around atmospheric values, used in most catalytic applications. The energetics of the butene plus hydrogen system on the platinum (111) system was estimated in both those extremes. First, the coadsorption Gibbs free energies ΔG_{coads}(nH+But) on Pt(111) and the adsorption energies

ΔG_{ads}(But) on nH@Pt(111) for the most stable configuration of each isomer (depicted in Figure 1) were calculated as a function of the H coverage for conditions that closely emulate those used in surface-science experiments: T=80 K, P=10^{-7} Torr, and a P_{H2}/P_{Butene} pressure ratio of 25.[35] The resulting energies are collected in Table 1. It is interesting to note that with the PBE-TS functional, the H atoms in the most stable coadsorbed systems in terms of the Gibbs free energy are mainly in fcc positions, and no longer all in a top site, in agreement with experiments.[52,53,54] On the contrary, the optPBE functional still favors systems with all H atoms on atop Pt sites, in disagreement with experiments (see also Figure S11). Moreover, according to those data, the *trans* isomer is more stable than the *cis* counterpart on Pt(111) surfaces with low hydrogen coverages. However, the *cis* isomer starts to show stronger adsorption at hydrogen coverages beyond five H atoms per calculating unit cell (θ_H = 0.56 ML). The difference in the coadsorption free energies between the *cis* and *trans* isomers at θ_H = 0.89 ML is 0.05 eV (1.2 kcal/mol) at the PBE-TS level, in agreement with the estimated experimental value of 1.8 kcal/mol.[35] It is worth noting that at 80K, this seemingly small coadsorption free energy difference corresponds to less than 0.1% of the *trans* isomer on the surface. The proportions of the *cis* and *trans* 2-butene coadsorbed with n H atoms as a function of temperature are shown in Figure S19. When nine H atoms are present, the system where the 2-butene molecule is physisorbed is the most stable.

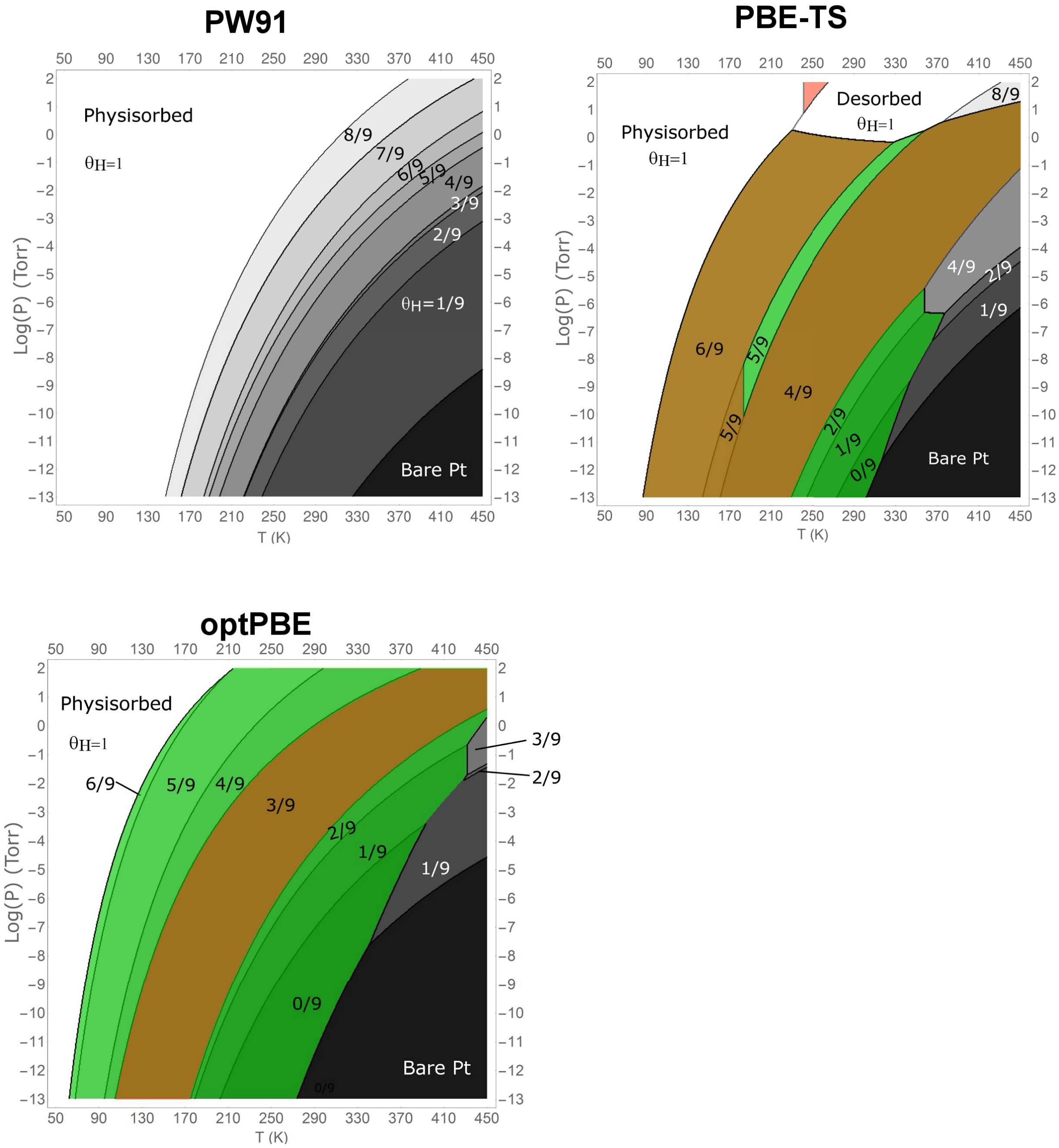


Figure 2: Thermodynamic stability of adsorbed 2-butene on platinum, with a P_{H2}/P_{Butene} pressure ratio of 25. Black: bare platinum; Green: *trans* 2-butene coadsorbed with hydrogen. $\theta_H = 0/9$ corresponds to the adsorption of 2-butene alone; Orange: *cis* 2-butene coadsorbed with hydrogen; Grey: Desorbed *trans* 2-butene with a H-covered Pt; White: physisorbed or desorbed *trans* 2-butene on Pt covered with 1 ML of H atoms. Pink: physisorbed *cis* 2-butene on Pt covered with 1 ML of H atoms.

Table 1: Coadsorption Gibbs free energies (ΔG_{coads}, eV, Equation 1) for *cis* and *trans* 2-butene with n H atoms on the Pt(111) surface and *cis* and *trans* 2-butene adsorption Gibbs free energies (ΔG_{ads}, eV, Equation 2) on a hydrogen pre-covered Pt(111) surface (with n H atoms). Only the most stable

structures are listed here. The calculations were done under high-vacuum pressure (10^{-7} Torr), at 80 K and for a P_{H2}/P_{butene} ratio of 25. (a) Physisorbed states.

	PBE-TS				optPBE			
	ΔG_{coads} on Pt(111)		ΔG_{ads} on nH@Pt(111)		ΔG_{coads} on Pt(111)		ΔG_{ads} on nH@Pt(111)	
n	*trans*	*cis*	*trans*	*cis*	*trans*	*cis*	*trans*	*cis*
0	-1.376	-1.363	-1.361	-1.348	-1.150	-1.136	-1.150	-1.136
1	-1.790	-1.769	-1.376	-1.355	-1.431	-1.411	-1.107	-1.088
2	-2.171	-2.151	-1.352	-1.331	-1.678	-1.653	-1.067	-1.041
3	-2.522	-2.507	-1.323	-1.307	-1.878	-1.926	-0.986	-1.034
4	-2.864	-2.872	-1.329	-1.337	-2.021	-2.015	-0.902	-0.896
5	-3.100	-3.080	-1.246	-1.226	-2.099	-2.073	-0.767	-0.741
6	-3.274	-3.285	-1.116	-1.127	-2.120	-2.118	-0.593	-0.591
7	-3.320	-3.334	-0.906	-0.920	-2.092	-2.078	-0.417	-0.403
8	-3.316	-3.368	-0.657	-0.709	-2.086(a)	-2.075(a)	-0.276(a)	-0.265(a)
9	-3.466(a)	-3.450(a)	-0.577(a)	-0.562(a)	-2.150(a)	-2.148(a)	-0.229(a)	-0.227(a)

Then the variation in coadsorption Gibbs free energies with temperature was calculated as well. Two sets of conditions were used. First, a low total pressure (10^{-7} Torr) with a P_{H2}/P_{Butene} pressure ratio of 25 was considered, as previously described. The resulting PBE-TS and optPBE profiles are similar: only the PBE-TS results are plotted in Figure 3 (top panel). For the sake of clarity, for each hydrogen coverage, only the most stable 2-butene isomer is shown. The full PBE-TS and optPBE graphs are shown in Figure S14 and Figure S16 (Supplementary Information). At such low pressure, 2-butene is physisorbed at low temperatures (up to 125 K with PBE-TS level, up to 90 K with optPBE). As the temperature increases, however, the 2-butene coadsorbed with 6 H atoms (black curve) becomes the most stable. The general trend is that higher temperatures favor a lowering of the coverage of the coadsorbed hydrogen: 2-butene desorbs around 380 K with PBE-TS and 325 K with optPBE. Interestingly, with PBE-TS, the most stable adsorbed isomer below 200 K is *cis* 2-butene. This is in agreement with the experimental results obtained by using infrared absorption spectroscopy, which show that the adsorbed *trans* isomer transforms to the *cis* isomer.[35,63] Our calculations also suggest that the hydrogen coverage in that study, which could not be determined experimentally, was likely to be around 0.44-0.56 ML (4-5 atoms per unit-cell), assuming that the system was under thermodynamic equilibrium. It is worth noting that in the absence of any hydrogen coverage, the *trans* isomer would always be the most stable one: a coverage of four or more hydrogen atoms is needed to favor the *cis* isomer. This is further shown in Figures S12, S13 and S19 (Supporting Information).

Surprisingly, our computations indicate that 2-butene is physisorbed at low temperatures, even if chemisorption has been reported in UHV experiments. [35,63] This comes from the fact that under the experimental conditions, the pre-dosed surface may not be at thermodynamic equilibrium. Indeed, as first noted by Ertl and coworkers, it is extremely difficult to adsorb a full monolayer of H atoms even under an atmosphere of H_2.[67] Lutterloh estimated that the maximum H coverage under these conditions may be less than 0.8 ML,[68] in which case one should discard the green and blue curves from our analyses: the *cis* 2-butene is then predicted to be coadsorbed with 7 hydrogen atoms, in good agreement with the experimental results.

The second set of conditions, at a higher pressure (1 bar) and a P_{H2}/P_{Butene} pressure ratio of 10, was considered to simulate the experimental conditions used in catalytic hydrogenations. The results are plotted as a function of temperature in Figure 3 (bottom panel). The relative positions of the various free energy curves are similar to the previous ones, calculated for the UHV experiments. However, the transitions between the various coverages occur at higher temperatures. For example, 2-butene is physisorbed until 260 K (185 K with optPBE) and desorbs at temperatures higher than 500 K (outside the plot). At the temperatures typically used in this catalysis, between 300 and 500 K, a coverage of between 0.66 (300 K) and 0.44 (500 K) ML in hydrogen is expected on the surface, roughly half a monolayer, in agreement with previous studies.[25,28,64] The *cis* isomer also appears to be slightly more stable on the Pt(111) surface than the *trans* counterpart under those pressures and temperatures.

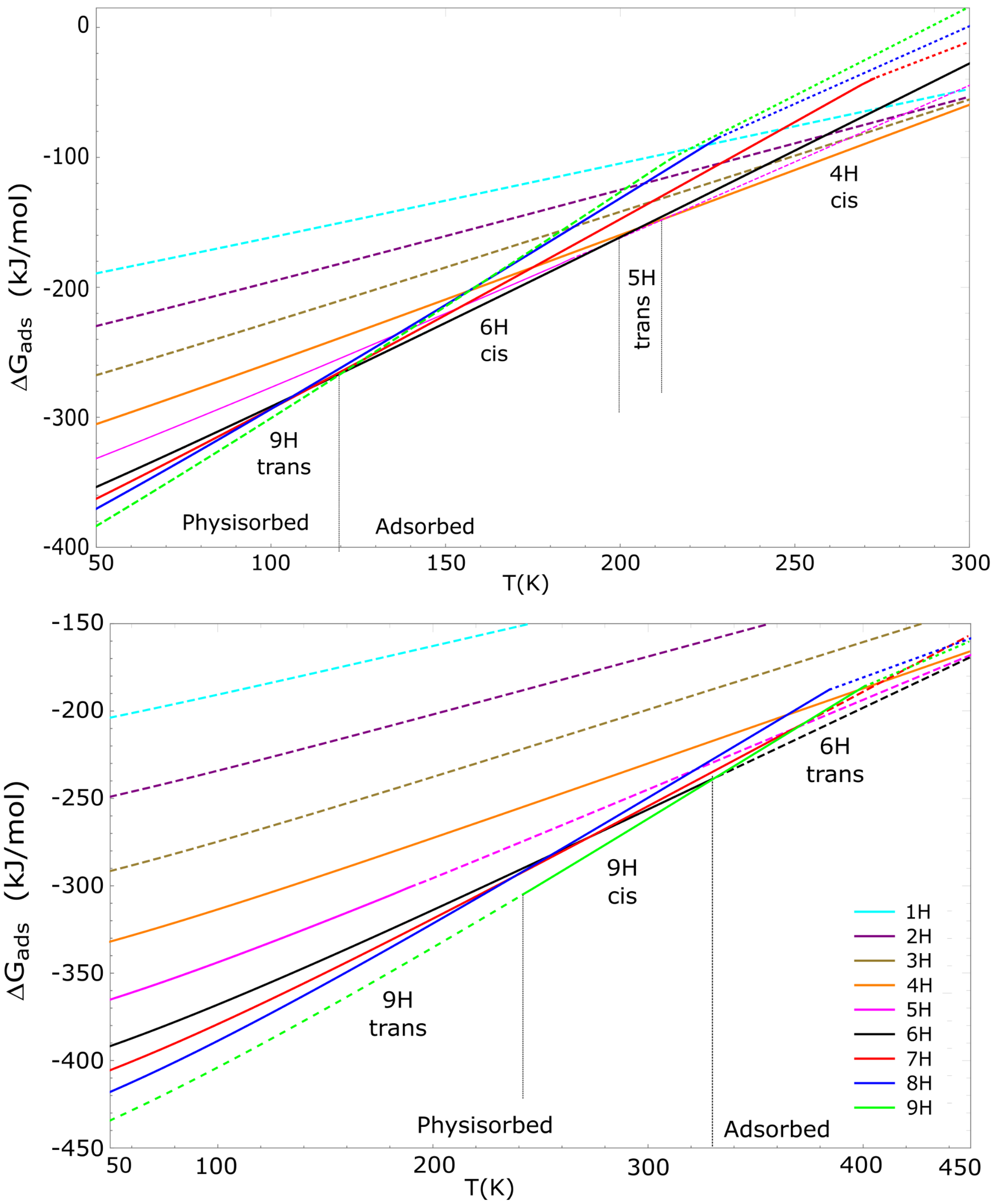


Figure 3: Simplified PBE-TS Gibbs free coadsorption energy diagrams of 2-butene coadsorbed with n H atoms as a function of the temperature at a pressure of 10^{-7} Torr and a constant pressure ratio P_{H2}/P_{butene} of 25 (top), and at a pressure of 1 bar and a constant pressure ratio P_{H2}/P_{butene} of 10 (bottom). The solid lines correspond to the adsorbed *cis* isomer, dashed lines correspond to the adsorbed *trans* isomer, dotted lines correspond to the desorbed *trans* isomer. For each coverage, only the most stable state is shown.

In summary, one of the main objectives of our work was to show that calculations such as those presented here allow for the estimation of the thermodynamics of adsorbed systems under realistic experimental conditions. It should be noted that the calculations reported above do not include the layer of alkylidynes that is known to be present on the surface under reaction conditions.[10, 69, 70] This is an effect that would need to be included in future calculations. Nevertheless, since coadsorbed hydrogen sometimes exerts a similar effect than those strongly carbonaceous deposits on the energetics of the adsorbed molecules,[71] it can still be concluded that our calculations provide a good qualitative picture of the trends expected in terms of the effect of the coadsorption of hydrogen and olefin on catalytic performance under realistic conditions.

Conclusions

The energetics of the adsorption of *cis* and *trans* 2-butene on Pt(111) in the presence of hydrogen has been evaluated for nine coverages of hydrogen, covering the range from 0.11 to 1.00 ML. The coadsorption free energy ΔG_{coads} of each isomer in its most stable adsorption structure has been calculated for all of those hydrogen coverages for two different situations: a total pressure of 10^{-7} Torr with a P_{H2}/P_{butene} pressure ratio of 25, as used in surface-science studies, and a total pressure of 1 bar and a P_{H2}/P_{butene} pressure ratio of 10, as used in catalytic reactions. The results obtained with functionals taking dispersion forces into account (PBE-TS and optPBE) have been compared with those obtained with pure DFT (PW91). Because it underestimates the butane adsorption energy, PW91 cannot reproduce the experimental results; the inclusion of dispersion forces is therefore mandatory. The diagrams representing the variation of ΔG_{coads} with temperature have similar shapes for PBE-TS and optPBE. However, the transition temperatures and the nature of the butene isomer depend on the functional used. Trends can nevertheless be extracted from the diagrams. At low temperature (below 110-120 K at low pressure and below 240 K at high pressure), 2-butene is physisorbed above a surface covered with one monolayer of hydrogen. When the temperature increases, 2-butene is coadsorbed first with 6 H atoms and then with 4 H. It means that, whatever the pressure used, when 2-butene is adsorbed, the hydrogen coverage adapts to reach values between 0.67 and 0.44, a range that can be related to the experimental maximal coverage in hydrogen when butadiene adsorption is considered.[50] Moreover, for some hydrogen coverages the *cis* isomer is more stable than the *trans* counterpart. For example, with PBE-TS, the *cis* isomer is the most stable over a large temperature and pressure domain, while with optPBE, the *cis* isomer is stable only with 0.33 ML of coadsorbed hydrogen. This result provides a good explanation for the *trans*-to-*cis* isomerization conversion seen experimentally under certain conditions.

Our results show that the DFT calculations that include the dispersion forces can help develop a good understanding of adsorbate systems both under ultra-high vacuum and catalytic conditions. They provide a theoretical framework to better explain the experimental results, particularly the unusual *trans*-to-*cis* isomerization of 2-butene, and can help experimentalists evaluate the state of the catalytic surface under realistic conditions.

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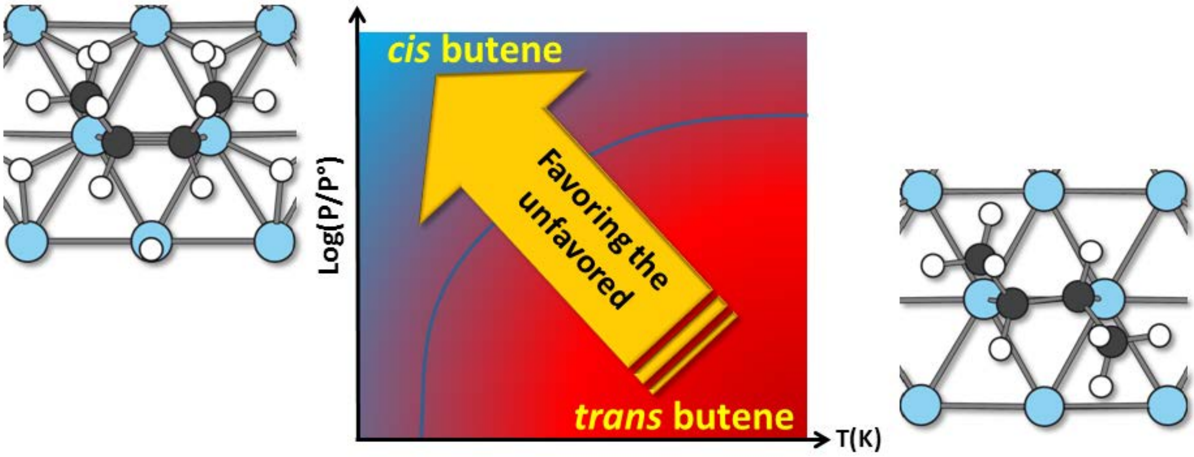

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respectively, a process that was carried out on the basis of the results obtained for the coadsorption of one H atom: the atoms were removed according to their ranking in terms of their calculated energies. The coadsorption of 2-butene with 2 and 3 H atoms was considered as well starting for the most stable conformations of 2-butene adsorbed with 1 H atom, and adding one (and then two) H atom according to their coadsorption energies. This procedure is detailed in the SI for the PW91 functional.

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