

The effect of substituents on the adsorption of alkenes on (111) Pt and Pd surfaces: a theoretical study

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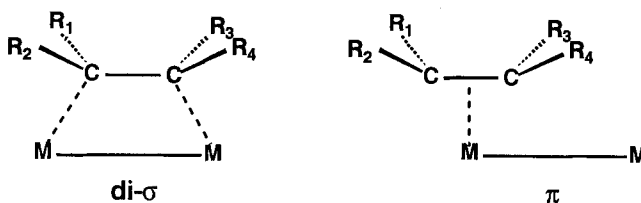
The coordination modes of ethylene, propene, 1- and 2-butenes, 2-methyl-2-butene, and styrene on a Pt(111) or a Pd(111) surface have been compared on the basis of extended Hückel calculations. The presence of methyl substituents induces a uniform decrease in the binding energies of the alkenes, both on Pt and on Pd. The phenyl group yields the same result on Pt but, on the contrary, gives a stronger adsorption mode on Pd. The interpretation of these results is based on the balance between attractive and repulsive interactions, the role of the latter being predominant. This trend in binding energy is related to the decrease of the hydrogenation reactivity of olefins upon substitution *in the case of a competitive reaction*.

Keywords: alkene adsorption; propene adsorption; butene adsorption; styrene adsorption; Pt(111) surface; Pd(111) surface; theory; Hückel calculation

1. Introduction

The chemisorption of unsaturated molecules on metal surfaces of group X elements is an important step of catalytic hydrogenation reactions, and has already been studied both experimentally, on model single crystal surfaces, and by theoretical approaches [1–3]. The case of olefins is of special interest. If ethylene adsorption is the center of several theoretical studies [1,4], little effort has been devoted to the study of substituted olefins, which are very important in a chemical aspect. Substituted olefins have been experimentally studied, and the data on 1-alkenes (propene, butene, pentene and isobutene) [5,6] and on 2-alkenes (cis and trans 2-butenes) [6] show that, even if these molecules are all di- σ bound to a Pt(111) surface, the desorption temperature slowly decreases upon substitution. These systematic changes of chemisorption of olefins, when they are substituted, have not been analyzed in details by molecular orbital analysis and this is the topic of this note. To our knowledge, the only related theoretical works deal with propene adsorption and α -hydrogen abstraction on Pt(111) [7] and with alkene adsorption on Pt(110) [8].

For this qualitative analysis on the influence of substituents, we use the semi-empirical extended Hückel method, the surface being modelled by a cluster of 49 atoms with a fcc structure exposing a (111) face. The spurious effect introduced by the edge of this finite cluster, as compared with an extended surface, is corrected with a special procedure. This procedure and the electronic parameters used for the calculation have been described elsewhere [1–3]. Two adsorption modes can be found for alkenes, a di- σ one where the molecule is bound to two metal atoms on the surface and a π one where only one metal atom is involved. Both have been observed experimentally on different metals or exposed faces (scheme 1).



Scheme 1.

Since the extended Hückel method is not fully appropriate for bond length optimization, standard values have been used. The metal–C distance is kept fixed at 2.1 Å; C–H = 1.085 Å; C–(CH₃) = 1.52 Å; C–C in Φ = 1.40 Å; C–C(Φ) = 1.50 Å. In both the di- σ and the π geometries, the molecule is hybridized upon adsorption, which means that the substituents on the C=C bond are tilted away from the surface, in order to improve the adsorption. This hybridization is a very important process for the adsorption and has already been described for ethylene [2–4]. In our calculations, this distortion of the molecule is introduced by a single geometric parameter h that controls a linear variation of all geometric coordinates between gas phase sp² carbons ($h = 0$; C–C = 1.34 Å; CCR = RCR = 120°) and a fully distorted ethane-like sp³ geometry ($h = 1$; C–C = 1.54 Å; CCR = RCR = 109.47°). Notice that the π geometry has always a smaller hybridization than the di- σ one. The calculated optimal hybridization for di- σ ethylene on Pt(111) is $h = 0.85$, which corresponds to a C–C bond length of 1.51 Å. This value is in good agreement with the experimental value (1.49–1.52 Å) [9].

Due to the approximation in the theory, calculated binding energies are not fully quantitative and, therefore, cannot be directly compared with the experimental values, even if they usually fall in a very satisfactory energy range (the calculated BE for ethylene on Pt(111) is 15 kcal/mol and the experimental value between 12 and 15 kcal/mol). However, the extended Hückel approach usually gives reliable trends in comparing related systems, even if the energy variations can be overestimated.

2. Adsorption of alkenes on Pt(111)

Only a small change of the optimum hybridization h has been found compared to ethylene, and as a consequence, h has been taken at 0.9 for di- σ , except for cis-2-

butene and 2-methyl-2-butene, and at 0.5 for π . For each molecule the best rotational conformation for the substituents has been obtained. The results for propene, 2-methyl-propene, trans-2-butene, 2-methyl-2-butene and styrene are given in table 1, together with ethylene, recalled for comparison. As previously explained, our analysis of the binding of unsaturated molecules on metal surfaces is based on the distinction between stabilizing two-electron and destabilizing four-electron interactions. The former are quantified in the calculation by the sum ET of the absolute values of the orbital electron transfers between the molecule and the cluster, either electron donation or back-bonding and involve the classical frontier orbital interactions. The latter come from the interaction between occupied orbitals on the molecule and occupied states on the surface: they are quantified by the squared overlaps between these orbitals summed over all occupied states of the molecule and the cluster (S^2). The binding energy BE reflects the balance between the two types of interactions.

The lecture of table 1 reveals that the substitution of the C=C bond leads to a regular decrease in binding energy, in qualitative agreement with the desorption experiments, even if the theoretical trend is somewhat stronger than the experimental one. The π_{CC} geometry remains less stable than the di- σ one, so that this form has not been calculated for the di- and trisubstituted ethylenes. The same trend of

Table 1

Binding energies (BE in kcal/mol), total electron transfers (ET in e^-) and $S^2 \times 10^2$ values for adsorption of alkenes on Pt₄₉(111)

	di- σ ($h = 0.9$)			π ($h = 0.5$)		
	BE	ET	S^2	BE	ET	S^2
CH ₂ =CH ₂	-15	1.40 $\left\{ \begin{array}{l} \pi \ 0.70 \\ \pi^* \ 0.65 \end{array} \right.$	9.03 ^a	-8	0.98 $\left\{ \begin{array}{l} \pi \ 0.52 \\ \pi^* \ 0.34 \end{array} \right.$	9.21 ^a
CH ₃ CH=CH ₂	-11	1.41 $\left\{ \begin{array}{l} \pi \ 0.72 \\ \pi^* \ 0.60 \end{array} \right.$	10.17	+1	1.07 $\left\{ \begin{array}{l} \pi \ 0.53 \\ \pi^* \ 0.33 \end{array} \right.$	11.21
(CH ₃) ₂ C=CH ₂	-6	1.46 $\left\{ \begin{array}{l} \pi \ 0.75 \\ \pi^* \ 0.56 \end{array} \right.$	11.28	^b		
CH ₃ CH=CHCH ₃ trans ^c	-7	1.49 $\left\{ \begin{array}{l} \pi \ 0.75 \\ \pi^* \ 0.57 \end{array} \right.$	11.26	^b		
(CH ₃) ₂ =CHCH ₃	-2	1.49 $\left\{ \begin{array}{l} \pi \ 0.78 \\ \pi^* \ 0.51 \end{array} \right.$	12.43	^b		
Φ CH=CH ₂	-9	1.73 $\left\{ \begin{array}{l} \pi \ 0.88 \\ \pi^* \ 0.56 \\ \pi_{\Phi} \ 0.18 \\ \pi_{\Phi}^* \ 0.02 \end{array} \right.$	11.89	-5	1.60 $\left\{ \begin{array}{l} \pi \ 0.75 \\ \pi^* \ 0.36 \\ \pi_{\Phi} \ 0.30 \\ \pi_{\Phi}^* \ 0.03 \end{array} \right.$	13.71

^a The difference observed for S^2 with the values given in ref. [1] is due to the consideration of all occupied orbitals (except the s orbitals) instead of only π_{CC} .

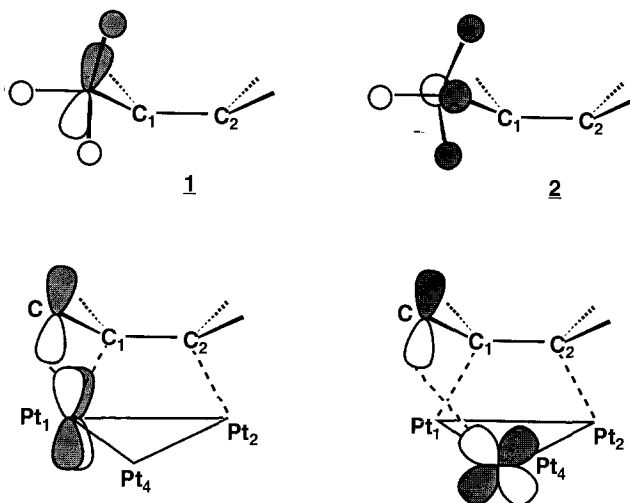
^b Not calculated because too much unstable.

^c BE for cis-2-butene is also -7 kcal/mol.

decreasing chemisorption with substituents has also been observed for aldehydes [3].

This weakening of the chemisorption is not obvious since methyl substituted ethylenes are better electron donors and since this electron donation is the main part of the two-electron interaction. The total electronic transfer indeed increases with substitution, with a significantly higher donation of the π orbital. The effect of the substitution of the hydrogens by methyls in ethylene is to shift up all the orbitals involved in the interaction with the surface, especially π_{CC} and π_{CC}^* , as shown in fig. 1. The π_{CC} orbital, being higher in energy, interacts better with vacant states of the cluster, and one effectively observes an increase in the electron transfer from π_{CC} with substitution. On the contrary, the π_{CC}^* orbital is moved further from the occupied d band which yields a decrease of the back-bonding interaction. However, taking into account all the molecular orbitals (especially those coming from lower lying occupied orbitals built from p_x or p_y), the net result is an increase of the stabilization coming from two-electron interactions, in contrast with the decrease in binding energy.

This comes from the fact that the destabilizing four-electron interactions are also increased upon substitution. The main reason is an additional repulsion originating from methyl-centered molecular orbitals. These repulsions have been analysed in detail for aldehydes and ketones [2,3], especially their decomposition into through-bond and through-space interactions. The orbitals involved in these repulsions between a methyl and the surface are the two π_{CH_3} orbitals 1 and 2 and some occupied d orbitals of surface Pt atoms. The largest interactions are between 1 and d_{yz} Pt₁ or d_{xz} Pt₄ and between 2 and d_{xz} Pt₄ (see scheme 2). As illustrated by the



Scheme 2.

COOP curves (crystal orbital overlap population) drawn in fig. 2, both the bonding and the antibonding contributions are located below the Fermi level and there-

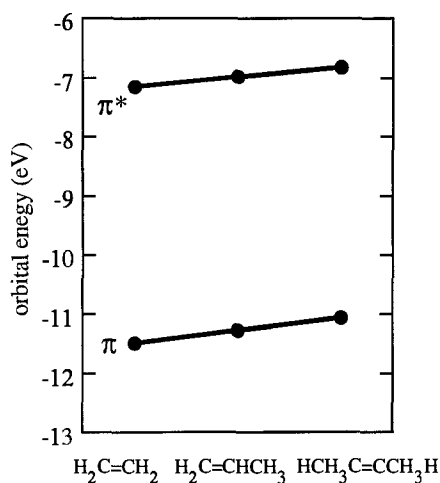


Fig. 1. Variation of the π and π^* frontier orbital energies upon substitution: ethylene, propene, and trans-2-butene in the gas phase geometry.

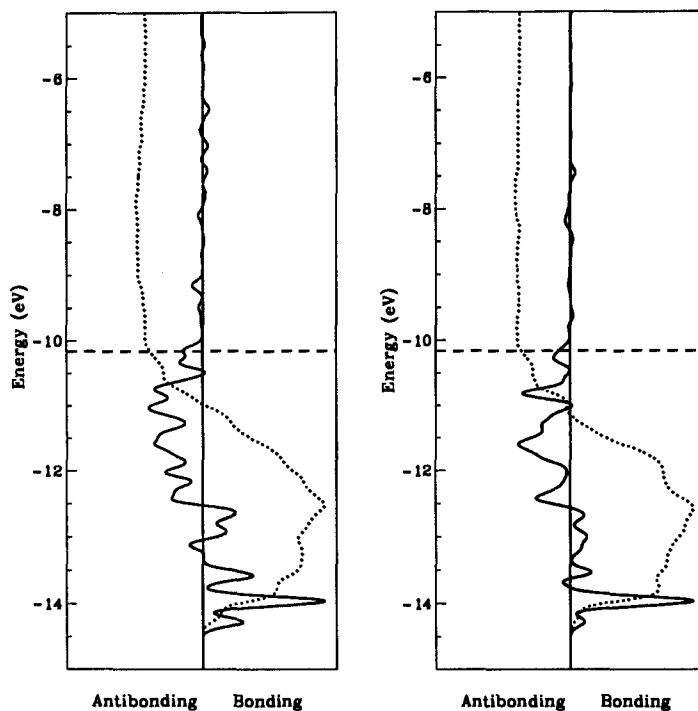


Fig. 2. COOP (crystal orbital overlap population) curves obtained for propene on Pt(111) in the di- σ geometry. Left: between d_{yz} Pt₁ and 1; right: between d_{xz} Pt₄ and 1. The dashed line represents the Fermi level.

fore occupied, which reveals a destabilizing interaction. This is similar to the classical two-orbital four-electron interactions.

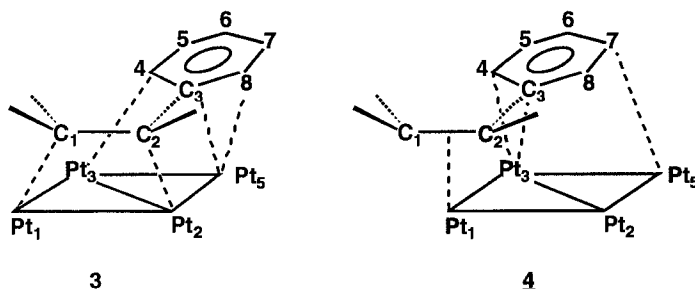
As a consequence, the change in binding energy results from a balance between the increase of both stabilizing and repulsive effects. In the calculation, the global trend is that the repulsion dominates, yielding a roughly uniform decrease of the binding energy for each additional methyl group, in agreement with the experimental trend for desorption temperatures. It should be noted that this influence of repulsive interactions seems to be slightly overestimated in the calculations.

Despite this global repulsive interaction between the methyl group and the surface, which can be illustrated by an overall negative CH_3 -surface overlap population (-0.041), there is one small attractive Pt-H interaction (overlap population 0.027) which indicates a possible dissociative adsorption leading to an allylic species as proposed by Anderson et al. [7].

The π geometry is more sensitive to these steric-like interactions, first because of the smaller hybridization and second because the substituents are closer to the neighboring metal atoms for geometrical reasons (see scheme 1). This repulsion can be partly released by a more pronounced tilt of the substituents from the surface. However, the π adsorption mode is even less favored for substituted olefins than it is for ethylene.

In the calculations, the 2-methyl-2-butene gives a very unstable adsorption mode on a Pt(111) surface. This is due first to an additional methyl-surface repulsion but also to an intramolecular steric hindrance between cis methyl groups due to the pyramidal conformation implied by adsorption. The same effect can be seen for cis-2-butene. It can be partly released by lengthening the C-C bond and decreasing the hybridization ($h = 0.8$). This would result in a longer C-C bond in adsorbed cis-butene than in trans-butene in agreement with spectroscopic data [10].

Until now, only alkyl substituents, modelled by a methyl group, have been considered. Unsaturated substituents can have somewhat different effects, as shown in the following for the case of styrene adsorption. Contrary to a methyl group, part of the interactions between the phenyl substituent and the surface are attractive, as shown by the positive overlap populations (0.012 , 0.011 and 0.060 for



Scheme 3.

Pt₅C₃, Pt₅C₈ and Pt₃C₄ respectively (3) (scheme 3). As a consequence, the phenyl group lies closer to the surface, compared to a methyl.

The approach of the substituent towards the surface is nevertheless stopped by the presence of accompanying electronic repulsions. Among the six π orbitals of the phenyl group, four have a non-zero coefficient on C₃ and therefore have a mixing with the π_{CC} and π_{CC}^* orbitals of the C=C bond: the electron transfers called π and π^* in table 1 include their contributions. The other two π orbitals of the phenyl ring (one occupied and one vacant) have a node on C₃ and therefore a much smaller mixing with the π system of the olefin. They have, however, a direct interaction with the surface, especially the occupied one which loses $0.18 e^-$ (noted π_Φ in table 1). This interaction mainly involves the d_{z^2} orbital of Pt₃ whose electronic population decreases by $0.25 e^-$ by an electronic process already described for other systems [2,3]: by interaction with π_Φ , d_{z^2} Pt₃ is shifted up in energy, some contributions of this orbital being pushed upon the Fermi level, and is therefore depopulated. The consequence of all these secondary interactions induced by the substituent is the large electron transfer found for styrene compared to other alkenes.

As seen previously [2,3], each attractive interaction with such a d^{10} metal is usually accompanied by a repulsive one. This explains the rather large S^2 value obtained for styrene, and the final moderate adsorption energy despite the strong electron transfer. The additional two-electron attraction and four-electron repulsion arising directly from the phenyl group can be estimated by artificially suppressing the orbital overlaps between the phenyl group and the surface. The binding energy becomes -15 kcal/mol, similar to that of ethylene itself, with $ET = 1.43$ and $S^2 = 9.19 \times 10^{-2}$. These values, compared with those of table 1, clearly show the influence of the phenyl ring in both the attractive and repulsive interactions.

Even if it is less strongly bound than the di- σ geometry, the π geometry for styrene is remarkably stable if compared with that of the other alkenes studied. For this adsorption mode, the substituents are close to the neighboring metal atoms, as explained before, but for a phenyl group this situation is on the contrary favorable and gives a better additional transfer from the phenyl ring than in the di- σ geometry ($ET(\pi_\Phi) = 0.30$ versus 0.18), reflected by the overlap populations Pt₃C₃ = 0.157 and Pt₃C₄ = 0.057 . The metal orbital involved in these interactions is again mainly d_{z^2} Pt₃ which loses $0.37 e^-$. In this adsorption structure 4 the Pt₃C₄ overlap population (compared to 0.25 for Pt₁C₁) and the Pt₃C₄ distance (2.36 \AA) imply a partial bond between Pt₃ and C₄. Therefore, geometry 4 is a kind of η_3 tri-hapto mode. The total electron transfer is more increased relative to ethylene, than in the di- σ geometry, but the four-electron interactions are also larger and the π_{CC} geometry remains less stable than the di- σ one.

3. Adsorption of alkenes on Pd(111)

The important point for the comparison between palladium and platinum for electronic structure calculations is that the Pd bulk has a slightly higher Fermi level

than Pt and a d-band width significantly reduced compared to the one of Pt, as seen from photoelectron data, which means that the radial expansion of the Pd d orbitals, almost fully occupied, is smaller than the one of the Pt d orbitals. As a consequence, the overlap of those d orbitals with the orbitals of the adsorbate is reduced on Pd. The direct result is that the four-electron interactions between molecule and surface are strongly decreased compared to the Pt case, as shown in table 2. On the other hand, the stabilizing two-electron interactions are also reduced. The first reason is again the smaller overlap, but the higher Fermi level also plays a role in the electronic transfer, resulting in a smaller decrease of back-bonding compared to donation transfer. The net result of these conflicting variations of repulsive and attractive interactions is a slightly more stable adsorption for ethylene. The adsorption forms with a higher S^2 are even more stabilized on Pd where the repulsions are released. The addition of substituents in that case only results in a small decrease of the binding energy, the 2-methyl-2-butene being still strongly adsorbed. This is even more the case for the π adsorption mode, especially sensitive to four-electron repulsions. As a consequence, on Pd the π adsorption becomes competitive with the di- σ one, especially for styrene where it is the most stable form. More generally the addition of substituents results in a much weaker decrease of the binding energy, compared with Pt. From the calculations, the ethylene molecule is less hybridized on Pd than on Pt [1], and the hydrogens are hence closer to the metal surface. However, the substituting methyl groups can easily accommodate this situation, due to the small repulsive interactions for that metal.

Styrene is a special case, since its adsorption energy is greater than the one of ethylene, especially for the π geometry. As seen before, the phenyl group has a tendency to approach the surface until the onset of four-electron repulsions. Since these interactions are smaller on Pd than on Pt, the phenyl ring can approach closer to the surface and this yields a rather strong additional interaction. Such a contact

Table 2

Binding energies (BE in kcal/mol), total electron transfers (ET in e^-) and $S^2 \times 10^2$ values for adsorption of alkenes on Pd₄₉(111)

	di- σ ($h = 0.7$)			π ($h = 0.5$)		
	BE	ET	S^2	BE	ET	S^2
$\text{CH}_2=\text{CH}_2$	-18	$1.11 \begin{cases} \pi & 0.52 \\ \pi^* & 0.57 \end{cases}$	4.78	-16	$0.74 \begin{cases} \pi & 0.38 \\ \pi^* & 0.30 \end{cases}$	5.03
$\text{CH}_3\text{CH}=\text{CH}_2$	-16	$1.12 \begin{cases} \pi & 0.54 \\ \pi^* & 0.52 \end{cases}$	5.61	-13	$0.80 \begin{cases} \pi & 0.38 \\ \pi^* & 0.28 \end{cases}$	6.63
$(\text{CH}_3)_2\text{C}=\text{CHCH}_3$	-13	$1.22 \begin{cases} \pi & 0.65 \\ \pi^* & 0.45 \end{cases}$	7.84	-5	$0.93 \begin{cases} \pi & 0.44 \\ \pi^* & 0.26 \end{cases}$	9.95
$\Phi\text{CH}=\text{CH}_2$	-22	$1.54 \begin{cases} \pi & 0.73 \\ \pi^* & 0.49 \\ \pi_\Phi & 0.22 \\ \pi_\Phi^* & 0.05 \end{cases}$	9.55	-27	$1.32 \begin{cases} \pi & 0.60 \\ \pi^* & 0.33 \\ \pi_\Phi & 0.25 \\ \pi_\Phi^* & 0.05 \end{cases}$	10.15

is facilitated by the smaller hybridization of the molecule on Pd. With a hybridization of $h = 0.35$ and a dihedral angle $C_4C_3C_2C_1$ of 20° (see 4), the Pt_3C_4 distance is 2.14 \AA , close to the standard value taken for a PtC bond (2.1 \AA). The Pt_3C_4 , Pt_3C_3 and Pt_5C_7 overlap populations are 0.118, 0.027 and 0.013 respectively. The d_{z^2} orbital of Pt_3 is strongly involved in the interaction and loses $0.48 e^-$. Like on Pt(111) the π_{CC} adsorption mode is in fact a trihapto geometry and is the most stable form on Pd(111). This result can be compared to the case of butadiene for which a tetrahapto di- π geometry is the most stable form on Pd(111), while a di- σ adsorption involving a single C=C bond is favored on Pt(111) [1].

4. Conclusion

The presence of alkyl substituents on the C=C bond gradually destabilizes the adsorption modes of ethylenic compounds on Pt(111) and, to a much smaller extent, on Pd(111). This result reproduces the experimental trends, although the decrease in the binding energies found by our calculations seems overestimated. Like for aldehydes and ketones [2,3], the variation of the attractive two-electron interactions cannot explain this evolution and would even give the inverse trend due to an enhanced donor capability of the substituted olefin. The key role is played by the four-electron repulsions which are increased upon substitution because of additional methyl-surface interactions.

This trend of decreasing binding energy with increasing substitution can be related to the hydrogenation reactivity of olefins in a *competitive reaction experiment*, which also decreases with the number of substituents of the double bond. A detailed kinetic study on a Pt/SiO₂ catalyst showed that this reactivity variation is not due to a change in the intrinsic hydrogenation rate constant but to a difference in the Langmuir adsorption constant [11]. This adsorption constant decreases strongly with increasing substitution, corresponding to a decrease of adsorption energy. The differences of binding energies estimated from these relative adsorption constants, with the same preexponential factor, are about half the calculated ones, which can be related to the overestimated four-electron repulsions, as discussed above. Therefore *the reactivity competition of olefins for hydrogenation*, when the substitution is increased, is mainly controlled by the adsorption step, which underlines the relevance of the experimental or theoretical studies of this elementary step.

Styrene is an interesting case. If the phenyl ring behaves somewhat like alkyls on Pt(111) and gives a less strongly adsorbed molecule than ethylene, the situation is totally different on Pd(111). On this surface, the phenyl ring takes an important part in the adsorption, yielding a kind of trihapto interaction. As a result, styrene in the π_{CC} geometry is the most strongly bound of the studied alkenes. It would be interesting to have experimental results on styrene adsorption in order to support our assumptions.

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