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LOW TEMPERATURE ADSORPTION OF ETHYLENE AND BUTADIENE ON PLATINUM AND PALLADIUM SURFACES: A THEORETICAL STUDY OF THE diσ/π COMPETITION

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The different low temperature coordination modes of ethylene and butadiene on a platinum (111) face, (110) face and on a palladium (111) face are compared on the basis of extended Hückel calculations. The nature of the chemical interaction between the olefin and the surface is detailed and the electronic factors that govern the coordination mode of the hydrocarbon are underlined. The different surfaces are modelled by a 49 or a 44 atoms cluster. A correction is applied in the calculation in order to minimize the artefact introduced by this cluster representation of an extended surface. For the adsorption, the respective importance of two electrons interactions and four electrons repulsions is the key point for the determination of the preferred mode. The di-σ coordination is more stable on platinum (111) but on the platinum (110) face the π coordination yields the same adsorption energy than the di-σ one. This is roughly the same result for the palladium (111) face. The π mode is there favored by a decrease of the four electrons repulsions caused either by a smaller number of metal neighbours for the surface atom (Pt(110)) or by a reduced radial expansion of the metal orbitals (Pd(111)). This π coordination is associated with a smaller hybridization of the ethylene molecule. The results are extended to the adsorption of butadiene and this allows a qualitative explanation of the better selectivity for butadiene partial hydrogenation on palladium compared with platinum.

Keywords: Ethylene adsorption on Pt theory, ethylene adsorption on Pd theory, butadiene adsorption on Pt theory, butadiene adsorption on Pd theory, Hückel calculation.

1. Introduction

The hydrogenation of unsaturated organic molecules is a very important process for industrial catalysis. In the most interesting case of a molecule with many chemical functions, the key point is not only to reach a high activity for the reaction but also to get a large selectivity in the specific hydrogenation of the desired unsaturated bond. The hydrogenation of acetylene or butadiene on palladium and platinum catalyst is an important example (scheme 1).

A very good selectivity for the partially hydrogenated product is obtained in the case of a palladium catalyst while a platinum one gives a higher amount of completely saturated molecules. Results for the hydrogenation of butadiene on

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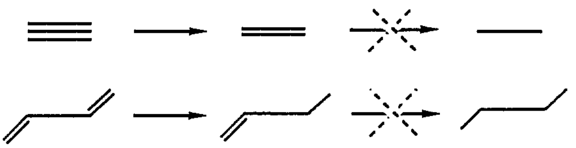


Scheme 1. Selective hydrogenation of acetylene and butadiene.

Table 1
Activity and selectivity for the hydrogenation of butadiene [1]

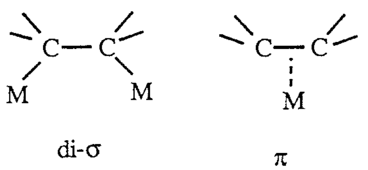
	Pt(111)	Pd(111)
TON s^{-1}	0.01	0.15
Selectivity in butene	58%	100%

platinum or palladium (111) single crystal face [1,2] are shown in table 1. The palladium surface is more active and much more selective in butene than the platinum one.

In order to give some insights for the understanding of such a difference of selectivity between the two metals, a first important step is to study the adsorption of the unsaturated molecule on the metallic surface. On the experimental side, the adsorption of ethylene has been the subject of a large number of studies on various metals. In the case of a low temperature non-dissociative adsorption, two coordination modes have mainly been proposed: the di-σ coordination where each carbon is linked to a different metal atom and the π one where a single metal atom is linked to the two carbon centers (scheme 2).

For the platinum (111) face there is a general agreement that the adsorption is di-σ with an adsorption energy ranging between 12 and 15 kcal/mol [3–6]. The ethylene molecule is distorted toward a nearly sp^3 geometry with a C–C bond distance of 1.49 Å [7]–1.52 Å [8,9] compared with the gas phase values of 1.34 Å for ethylene and 1.54 AaO for ethane. Things are different on the open (110) surface, reconstructed or not, where electron energy loss spectroscopy supports a coordination with a smaller distortion of the olefin assumed to be of the π geometry [10,11]. A mixture of di-σ and π coordinations is found in some cases [10,11].

Such a weakly distorted ethylene adsorbate is also found on palladium surfaces but both on the (111) and (110) faces [3,8] by EELS [12], NEXAFS and UPS [13]. For ethylene on palladium (111), NEXAFS gives a C–C bond distance of 1.43 Å



Scheme 2. The di-σ and π coordination of ethylene on a metal surface.

[13] and, separately, the C–C bond order has been evaluated to be 1.7 [3]. This π coordination may also coexist with di-σ adsorption on Pd(110) as shown by EELS [3]. The adsorption energy of ethylene on palladium is measured to be between 13 and 16 kcal/mol [3,23].

Therefore, there seems to be an important difference for the adsorption of ethylene on platinum and on palladium. The π geometry, favored by the second metal can only be obtained on platinum with the open (110) plane.

The knowledge on the chemisorption of butadiene is not so extensive. On Pt(111) a di-σ coordination, where only a double bond is involved, has been concluded from EELS experiments [14,15]. On palladium (111) preliminary studies suggest a completely different di-π adsorption that uses the two double bonds [16].

On the theoretical side, most of the studies also focus on the adsorption of ethylene on Pt(111) [17,20] and all support the di-σ coordination. The (110) face of platinum has already been studied [21] but the di-σ geometry is found to be the most stable conformation for ethylene in disagreement with experimental results. Tight-binding band-structure calculations were used by Baetzold [22] to study chemisorbed ethylene and butadiene on transition metals. Only d-orbitals were considered on the metals and the number of d electrons was varied. The predicted adsorption energies with this method were found to be not very reliable [22], especially for the π coordination. Metals with the same number of d electrons, as platinum and palladium, were not compared.

In the present paper, a theoretical study on the low temperature adsorption of ethylene and butadiene on Pt(111), Pt(110) and Pd(111) faces will be presented. The different chemisorption behaviors of these systems will be analysed, the nature of the chemical interaction between the olefin and the surface will be detailed and the electronic factors that govern the coordination mode of the hydrocarbon will be underlined. The theoretical model used in the calculations will be briefly introduced in section 2. The adsorption of ethylene and butadiene will be respectively studied in the sections 3 and 4. In the case of butadiene, the results obtained on the chemisorption will be applied for a qualitative analysis of the selectivity difference of palladium and platinum for the hydrogenation reaction.

2. Theoretical model

In our calculations, the extended surfaces of the metals are described by clusters. In order to get a correct description of the environment of the surface atoms, these clusters are generated by two neighbour metal atoms on the surface and may incorporate all the first neighbours ($N = 15$), all the second neighbours ($N = 49$) or all the third neighbours ($N = 114$) of these two atoms that will be directly involved in the chemisorption phenomenon. N is the size of the resulting

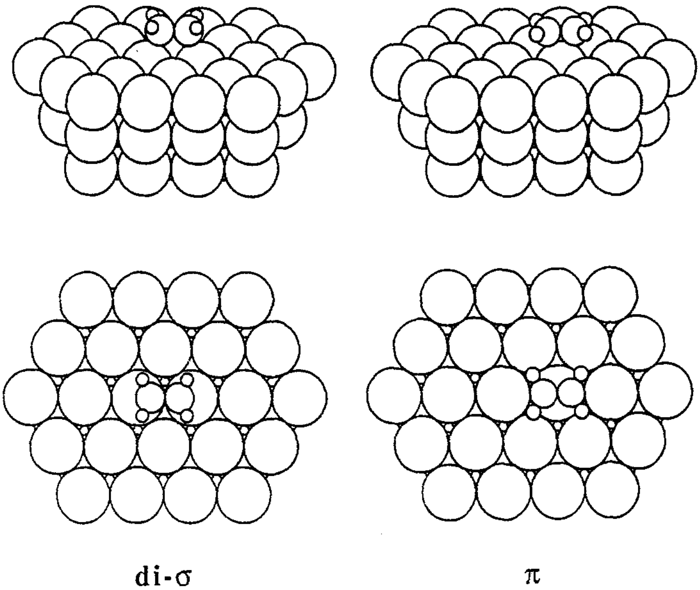
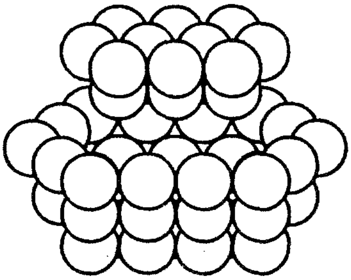


Fig. 1. Side view and top view of di-σ and π coordinations of ethylene on the 49 atoms cluster that models the (111) face of fcc platinum (or palladium).

semi-elliptic like cluster and the 49 atoms one is represented together with ethylene in fig. 1.

Extended Hückel calculations are performed on these clusters. The electronic parameters for carbon, hydrogen, platinum and palladium have been carefully chosen in order to get a coherent description of the electronic structure. More precisely, the parameters of platinum have been taken from the literature [17] and those of palladium have been comparatively determined on the basis of the following two electronic criteria. By reference to workfunction measurements, the Fermi level of palladium has been fixed 0.2 eV higher than the Fermi level of platinum. From XPS spectroscopy, the d-band width of palladium appears to be roughly the half of the d-band width of platinum. The chosen parameters of palladium, that verify these two properties, are shown in appendix. For carbon and hydrogen the atomic energies have been shifted up from standard values in order to simulate self-consistency and to give a small charge transfer between the olefin and the surface.

The modeling of an extended surface by a finite cluster always introduces artefacts in the calculation due to the presence of edge atoms. Only the atoms in the innerpart of the cluster are in a correct environnement, the outermost shell being higly unsaturated. In the case of electron rich metals as group VIII elements, this artefact results in an accumulation of electrons in the partially coordinated outer shell. This effect is especially strong with the extended Hückel method where there is little driving force in opposition to this charge transfer.



Scheme 3. Partition of the 49 atoms cluster into core part and outer shell. The core part has been pushed up.

These edge effects have been corrected in our calculations in the following way. The atoms in the cluster are sorted into the core part and the outer shell. This partition is illustrated in scheme 3 for the 49 atoms cluster.

In order to avoid the accumulation of electrons on the edge, the charge is renormalized on the core part. First the molecular orbitals of the entire cluster are projected on the core part, then a fractional filling of each molecular orbital is performed according to its weight on the core and this filling is stopped as soon as the electroneutrality of the core is reached. In other words what we do is a calculation of the core fragment directly embedded in the outer shell.

The influence of this correction on the convergence with cluster size of the charge on the surface platinum atom and the ethylene adsorption energy is shown in table 2. The surface atom being less coordinated than the bulk ones, it should present in the case of platinum a small excess of electrons. This is not at all the case without the correction where the electrons are attracted toward the even less coordinated atoms on the edge of the cluster. This incorrect electronic deficit on the surface is only very slowly corrected with increasing cluster size and the right small excess of electrons would only be achieved with very large clusters, unrealistic for the computation.

On the contrary, this charge on the surface has the good behavior when the correction is applied and even with small clusters. The need of a fair description of this electronic charge on the surface is obvious for the study of chemisorption.

Table 2

Charge on the surface platinum atom and ethylene adsorption energy for the corrected (C) and non-corrected (NC) clusters as a function of cluster size

	Charge on surface platinum		Ethylene adsorption energy (kcal/mol)	
	C	NC	C	NC
$N=15$	0	+0.33	20.3	17.9
$N=49$	−0.105	+0.27	15.3	20.0
$N=114$	−0.122	+0.17	14.6	18.2

The only slight difference between the 49 and the 114 cluster illustrates the much improved convergence with size of the electronic properties. This is also the case for the adsorption energy of ethylene where the 49 and 114 clusters differ by less than one kcal/mol if the correction is applied. Notice that the non-corrected clusters give a significantly stronger adsorption energy. Due to the good convergence with size, the following calculations have been performed with the 49 corrected cluster.

3. Adsorption of ethylene

3.1. ON THE PLATINUM (111) FACE

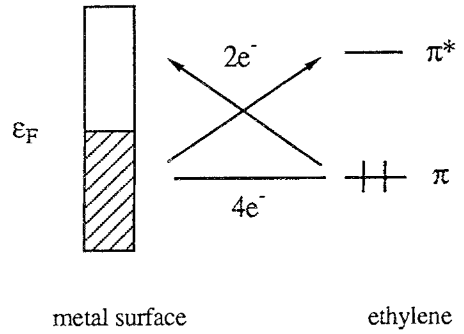
The di-σ and π coordination modes of ethylene on the Pt_{49} cluster that simulates the (111) face are illustrated in fig. 1. In both cases the molecule is not in its gas phase geometry but is distorted toward an sp^3 structure. This distortion of ethylene has been included in the calculation by mean of a single parameter h that indicates the hybridization between the gas phase sp^2 geometry ($h = 0$) and the fully sp^3 hybridized ethane geometry ($h = 1$). The variations of bond lengths, angles and dihedral angles between these two extreme positions are assumed to be linear with respect to the h parameter. The Pt–C bond distance has been kept fixed to 2.1 Å.

The optimum distortion and the related adsorption energy for both coordination modes are shown in table 3. Both geometries are found to give a stable adsorption but the di-σ one, with a high hybridization, is favored in agreement with previous experimental and theoretical studies. The calculated C–C bond length is 1.51 Å for the di-σ and 1.44 Å for the π coordination. This C–C distance and the adsorption energy for the di-σ situation compares well with experimental data. The orbital factors that govern the interaction are illustrated on scheme 4.

The electronic interaction between the ethylene molecule and the metallic surface can be divided into two components: the two electrons ones between the π orbital (resp. the π^* orbital) and the vacant bands (resp. the occupied bands) of the metal and the four electrons ones between occupied energy levels on both sides. The two main electronic factors that control these interactions are the

Table 3
Optimal hybridization and corresponding adsorption energies for the di-σ and π coordination modes of ethylene on Pt(111)

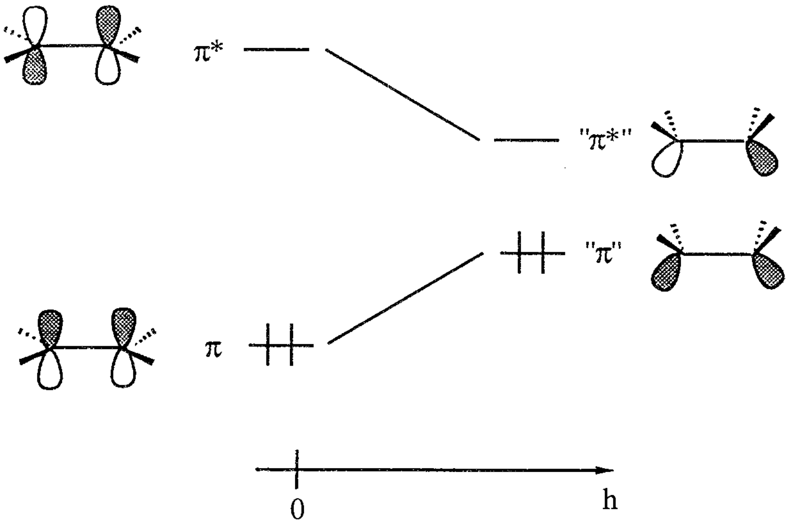
	di-σ	π
h	0.85	0.50
ΔE (kcal/mol)	15	8



Scheme 4. Two electrons and four electrons interactions between the surface and the ethylene molecule.

energy position of the π and π^* orbitals with respect to the metal Fermi level ϵ_F and their overlaps with the surface metal atoms orbitals. The hybridization distorsion has an important influence on these two electronic factors and therefore on the adsorption.

First, it destabilizes the isolated ethylene molecule resulting in a distortion energy that favors in any case the planar geometry. Upon adsorption, this first effect is counterbalanced by the energy levels factor: the π and π^* orbitals get closer to the metal Fermi level as h increases. This improves the two electrons interactions and hence favors the fully hybridized geometry. The situation is somewhat more complex if the overlap factor is considered. In the case of the di-σ coordination the two platinum atoms are in outer position compared to the C–C bond and therefore the overlap increases with h which leads to a stronger interaction. On the contrary, the platinum atom is just below the C–C bond in



Scheme 5. Influence of hybridization on the π and π^* orbitals.

the π coordination, the hybridization decreases the overlap, by rotating the π and π^* orbital lobes, and this weakens the interaction.

Then the orbital energy and the overlap factors follow the same trend for the di-σ case, while they fight each other for the π case when the hybridization is increased. It follows that the di-σ situation gives a strong interaction and a strong distortion of the molecule while the π situation is the one of small distortion and small interaction. The analysis of the result for Pt(111) is then straightforward if only two electrons interactions, that are stabilizing, are taken into account. However we will show in this article that the four electrons interactions play an important role in the di-σ/π competition. Indeed these interactions are destabilizing and hence they prefer the weak overlap situation, i.e. the π coordination.

The optimization of the adsorption energy for ethylene on a metal surface is a compromise between the search for increased two electrons interactions that yield the di-σ situation with high h and the decrease of the four electrons interactions that drives toward the π situation with low h. In order to understand the balance between these two effects a more quantitative analysis is needed.

Two electrons interactions are easy to quantify since they are associated with electron transfers. This is not the case for the four electrons interactions but, with a perturbation theory approach, they are proportionnal to the square of the overlap between the two interacting orbitals. The following integral was therefore used as a criterion for the repulsion strength,

$$I = \int_{E_b}^{\epsilon_F} S^2(E)\,\mathrm{d}E$$

where $S(E)$ is the overlap of the π orbital of ethylene with the surface molecular orbital of energy E, E_b is the energy of the bottom of the metal band and ϵ_F the Fermi level.

The electron transfers and the repulsion criterion are shown in table 4 for Pt(111). As explained before the two electrons interactions, especially the one from the occupied metal band toward the π^* orbital of ethylene, are stronger in the di-σ coordination. In the π mode the four electrons interactions are slightly smaller but in this case of Pt(111), this decrease of the repulsion is not big enough to compensate the two electrons interactions difference. As a result the di-σ coordination is clearly favored in this case. However this balance between

Table 4
Electron transfers and four electrons repulsions for ethylene on Pt(111)

Coordination	Electron transfers		Four electrons repulsions I×100
	π	π^*	
di-σ	−0.70	0.68	6
π	−0.52	0.34	5.6

attractive and repulsive interactions might be modified by a change of the crystal face or a modification of the metal nature, as it will be detailed in the following.

3.2. ON THE PLATINUM (110) FACE

The non-reconstructed (110) face of platinum has been modelled by a 44 atoms cluster with the correction of the edge effects previously described. The three adsorption geometries considered here for ethylene are shown in fig. 2. The (110) face is more opened than the (111) and its geometry can be described by means of metal atoms rows. These atomic rows on the first layer are not at contact distance and hence the rows in the second layer may be accessible for adsorption. However these adsorptions on the second layer have been calculated to be largely less favored than those on the first layer rows that will only be considered in this paper.

Similarly to the (111) face, a di-σ coordination and a π coordination have been considered on the first layer row. However, because of the anisotropy on the surface, there are two significantly different positions for the π coordination, one with the C–C bond parallel with the atomic row labelled $\pi(\parallel)$ and one with the C–C bond perpendicular to the row labelled $\pi(\perp)$.

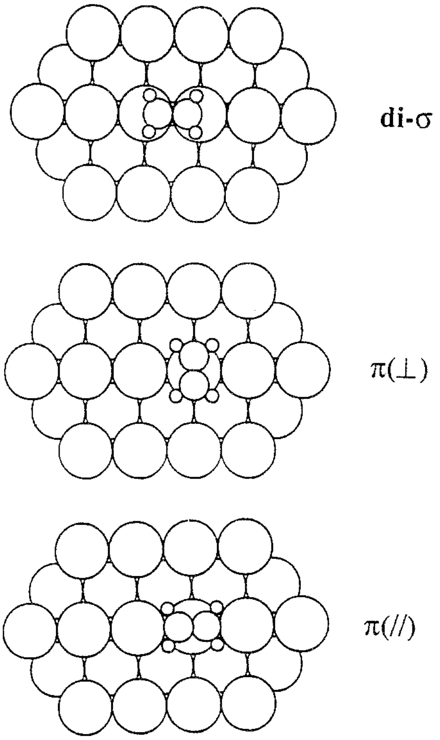


Fig. 2. top view of di-σ, $\pi(\perp)$ and $\pi(\parallel)$ coordinations of ethylene on the 44 atoms cluster that models the (110) face of fcc platinum.

Table 5
Optimal hybridization h and corresponding adsorption energies for the di-σ and π ($\perp$) and $\pi(\|)$ coordination modes of ethylene on Pt(110)

	di-σ	$\pi(\perp)$	$\pi(\|)$
h	0.85	0.40	0.40
ΔE (kcal/mol)	19	19	15

The optimized hybridizations and adsorption energies are shown in table 5. The di-σ geometry is slightly stabilized with the same optimal hybridization compared to (111). For the π mode however the increase of the adsorption energy is much larger and this low distorsion position is for the perpendicular case as stable as the di-σ coordination. The method of calculation is not enough quantitative to decide between the two forms. The result that the two geometries have an equivalent energy for the calculations compares well with some adsorption experiments [10,11] that yield a mixture of di-σ and π bound ethylene on the (110) face. The C–C distance is again 1.51 Å for di-σ and 1.42 Å for the π geometry.

The parallel π position is less favored. It should be noted that, to our knowledge, it is the first time that the perpendicular geometry is considered in calculations and that the previous study on Pt(110) by Maurice et al. [21] only compared di-σ with $\pi(\|)$. This clearly explains their conclusion of a preferred di-σ coordination in opposition with experimental results.

This more stable π position on the (110) face is in a counter intuitive manner associated with a less distorted molecule compared with the (111) case. This indicates that the level of hybridization of ethylene is not directly correlated with the strength of adsorption, in opposition with the qualitative rule generally assumed for the analysis of vibrational spectroscopy [12].

If we now look at the electron transfers and four electrons repulsions given in table 6, we see that the two electrons interactions are weaker on the (110) face than on the (111) one even if the adsorption is stronger. The smallest distortion of ethylene on (110) is a clear consequence of these reduced two electrons interactions. In this case, the four electrons repulsions play an important role for the final adsorption energy. Indeed these repulsions are much smaller on the (110) face, especially for the $\pi(\perp)$ conformation where the largest adsorption energy

Table 6
Electron transfers and four electrons repulsions for ethylene on Pt(110)

Coordination	Electron transfers		Four electrons repulsions I×100
	π	π^*	
di-σ	−0.67	0.70	5.2
$\pi(\perp)$	−0.44	0.30	3.9
$\pi(\|)$	−0.48	0.28	4.8

difference is found compared to (111). On the (110) face the weak interaction π position is therefore favored because it efficiently reduces the four electrons interactions, while it is still associated with smaller two electrons transfers compared to di-σ. The smaller distortion on the ethylene is hence linked to a decreased interaction but not to a decreased adsorption energy since not all the interactions components are attractive.

The four electrons repulsive interactions happen between the occupied part of the metal band, which is mainly of d character, and the ethylene π orbital. In group VIII metals the d band is nearly filled and therefore the d electron density at the surface is high which explains the importance in that case of four electrons repulsions for the interaction of an adsorbate.

For the (111) case the surface platinum atom has nine metal neighbours, while it has only seven in the case of (110) and this results in a more narrow d band in the local density of states on this surface atom. This loss of neighbour interactions compared to (111) therefore explains that the ethylene feels less repulsion from the d electrons on the surface. In the case of the $\pi(\|)$ geometry the carbon $2p_z$ orbital has a small overlap with first neighbours platinum atoms on the metal row. For the perpendicular orientation this secondary interaction is absent and this yields a further reduction of the four electrons interactions.

3.3. ON THE PALLADIUM (111) SURFACE

The second experimental way to modify the coordination of the ethylene is to switch to palladium. The adsorption energies and optimal hybridizations are shown in table 7. The results are much similar to the Pt(110) face. The π mode is strongly stabilized with a smaller distortion. The di-σ geometry is moderately favored compared to Pt(111) with also a significant decrease of distortion. The only difference is quantitative: the di-σ form is still more stable but only for two kcal/mol which is really at the limit of accuracy of the method of calculations. However the decrease of hybridization for both coordinations is consistent with the experimental evidence of a smaller distortion of ethylene on palladium. The π mode becomes competitive with the di-σ, which is very different from the results on platinum. The calculated C–C bond length are 1.48 Å for di-σ and 1.41 Å for π coordination, with the NEXAFS experimental value of 1.43 Å.

Table 7
Optimal hybridization and corresponding adsorption energies for the di-σ and π coordination modes for ethylene on Pd(111)

	di-σ	π
h	0.70	0.35
ΔE (kcal/mol)	19	17

Table 8
Electrons transfers and four electrons repulsion for ethylene on Pd(111)

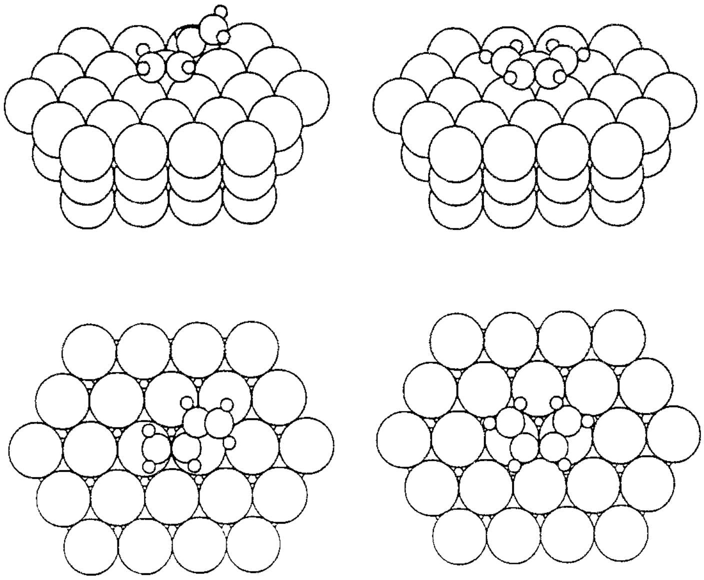
Coordination	Electron transfer		Four electron repulsions I×100
	π	π^*	
di-σ	−0.51	0.57	3.25
π	−0.38	0.27	2.8

The electron transfers and repulsions in table 8 for Pd(111) follow also the same trends. The two electrons interactions are markedly weakened together with a strong decrease of four electrons interactions compared to Pt(111). If we recall the electronic properties of palladium compared with platinum that were used to build the extended Hückel parameters, we see that the d bandwith of palladium is half the one of platinum with a nearly equal lattice parameter. This means that the radial expansion of the metal orbitals is significantly smaller for palladium. As a consequence the overlap with the orbitals of ethylene is reduced and both the two electrons and four electrons interactions are weakened. As explained before, the π coordination is more stabilized by that process because it takes advantage of the reduced four electrons repulsion.

4. Adsorption of butadiene

A di-σ and a di-π geometries have been considered for the adsorption of butadiene on platinum and palladium (111) faces (see fig. 3). The di-σ geometry only involves one of the two double bonds and is very similar to the ethylene di-σ coordination, except that one of the hydrogens is substituted by a vinyl group that only has a weak interaction with the surface. A quadri-σ type coordination that would use all the carbon atoms is impossible for geometric reasons. If a π type of interaction is considered the involvement of both double bonds on two metal neighbours is on the contrary geometrically possible (di-π coordination). In both cases adequate distortions of the butadiene frame are considered through a geometric movement controlled by a single parameter h. The following optimized hybridization and adsorption energies are given in table 9.

The result for di-σ is very similar to the ethylene case: the substituent effect is small. For the di-π coordination, the hybridization is slighty higher than the π geometry of ethylene and, more important, the adsorption energies are roughly doubled. This is in a sense natural since now the unsaturated molecule is linked to the surface by its two double bonds. For the Pt(111), where the π ethylene is less stable than the di-σ one, the di-π coordination of butadiene has now approximatively the same adsorption energy as di-σ. On the Pd(111) surface, π



di-σ di-π

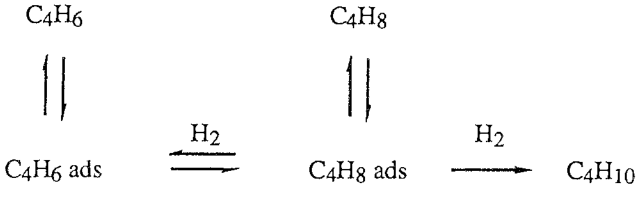
Fig. 3. Side view and top view of di-d and di-π coordinations of butadiene on the 49 atoms cluster that models the (111) face of fcc platinum (or palladium).

Table 9
Optimal hybridization and adsorption energy for the di-σ and di-π coordinations of butadiene on Pt(111) and Pd(111)

	Pt(111)		Pd(111)	
	di-σ	di-π	di-σ	di-π
h	0.85	0.60	0.65	0.50
ΔE (kcal/mol)	15	18	20	36

and di-σ ethylene are comparable and then the di-π geometry for butadiene is strongly favored.

This difference between platinum and palladium for the adsorption of butadiene may have important consequences in the hydrogenation reaction. The global mechanism generally considered in this case involves the following steps.



Scheme 6. General mechanism of butadiene hydrogenation.

The key point for this reaction to be selective in butene is, when adsorbed butene (C_4H_8ads) is formed, to orient the reaction toward its desorption instead of further hydrogenation to butane. As long as the adsorption energies are concerned, butene is very similar to ethylene or to di-σ butadiene. Therefore, on platinum (111), the adsorption energies of butene and butadiene are in the same range. As explained before, this is not at all the case for palladium (111) where butadiene in the di-π coordination is much strongly adsorbed than butene.

This energetic factor has an important influence on the competitive adsorption of butadiene and butene in the reaction. This competition with butadiene is the driving force for butene desorption on the palladium (111) face. This explains the high selectivity in butene of this palladium catalyst while the platinum, for which the adsorption energies are equivalent, yields a mixture of products. This interpretation is in agreement with experimental results and analysis [2].

5. Conclusion

The adsorption of ethylene on a metallic surface is controlled by a subtle balance between attractive two electrons interactions and repulsive four electrons ones. These repulsive effects come from the interaction between occupied orbitals on the molecule and the occupied part of the d-band. They are therefore especially important for group VIII metals which present a nearly complete filling of this d-band.

In the case of platinum (111), however, the preferred geometry is controlled by the two electrons interactions and is the di-σ strongly hybridized coordination. The weak interaction π mode can be favored by a decrease of the four electrons repulsions that can be achieved either on the platinum (110) face or the palladium (111) face. In these cases, the repulsion is weakened either by a smaller number of metal neighbours for the surface atom (Pt(110)) or by a reduced radial expansion of the metal atomic orbitals (Pd(111)). This π adsorption situation of low two electrons and low four electrons interactions is associated with a smaller hybridization of the molecule since the perturbation of the ethylene molecule is weaker.

This is a clear illustration of the fact that the most stable coordination for an adsorbate is not always the one associated with the strongest interaction, due to the repulsions. These four electrons interactions may also play an important role in decreasing the adsorption energy in order to get the optimal moderate adsorption needed for a good catalytic turnover. It can be noted that they are especially important for group VIII metals, which are among the best catalysts for many reactions.

In the case of butadiene, the entire π system can be only involved with a di-π coordination which is consequently favored compared to the single double bond di-σ mode. On Pt(111) the energy of the di-π geometry is equivalent to the energy of di-σ, while it is much higher in the case of Pd(111). The consequences of these differences on the competitive adsorption of butadiene and butene on Pt(111) and Pd(111) have been detailed. This yields a qualitative interpretation of the better selectivity, for the partial hydrogenation giving butene, of palladium catalysts compared to platinum ones.

Appendix

Parameters for the Extended Hückel calculations

atom	orbital	*Hii* (eV)	ζ_1	ζ_2	C_1	C_2
H	1s	−12.1	1.3			
C	2s	−19.9	1.625			
		−9.9	1.625			
Pt	6s	−9.29	2.544			
	6p	−4.48	2.544			
	5d	−11.26	6.013	2.696	0.6333	0.5512
Pd	4s	−7.905	2.19			
	4p	−2.362	2.152			
	5d	−10.51	5.983	2.613	0.5535	0.6701

References

[1] J. Masardier, J.C. Bertolini and A. Renouprez, *Proc. 9th Int. Conf. in Catalysis*, Calgary 1988, Vol. 3, p. 1222.

[2] T. Ouchaib, J. Massardier and A. Renouprez, J. Catal 119 (1989) 517.

[3] N. Sheppard, Ann. Rev. Phys. Chem. 39 (1988) 589.

[4] a) M. Salmeron and G.A. Somorjai, J. Phys. Chem. 86 (1982) 341;
b) R.J. Koestner, M.A. Van Hove and G.A. Somorjai, J. Phys. Chem. 87 (1983) 203.

[5] B.J. Bandy, M.A. Chesters, D.I. James, G.S. McDougall, M.E. Pemble and N. Sheppard, Phil. Trans. R. Soc. Lond. A 381 (1986) 141.

[6] J.C. Bertolini and J. Massardier, in: *The Chemical Physics of Solid Surfaces and Heterogeneous Catalysis*, eds. D.A. King and D.P. Woodruff, Vol. 3 (Elsevier, Amsterdam, 1984) 107.

[7] J. Stohr, F. Sette and A.L. Johnson, Phys. Rev. Lett. 53 (1984) 1684.

[8] J.E. Demuth, Surf. Sci. 84 (1979) 315.

[9] J.E. Demuth, IBM J. Res. Dev. 22 (1978) 265.

[10] E. Yagasaki and R.I. Masel, Surf. Sci. 222 (1989) 430.

[11] E. Yagasaki and R.I. Masel, Surf. Sci. 226 (1990) 51.

[12] J.A. Gates and L.L. Kesmodel, Surf. Sci. 120 (1982) L461.

[13] L.P. Wang, W.T. Tysoe, R.M. Ormerod, R.M. Lambert, H. Hoffmann and F. Zaera, J. Phys. Chem. 94 (1990) 4236.

[14] M. Abon, J.C. Bertolini and B. Tardy, J. Chim. Phys. 85 (1988) 711.

[15] N.R. Avery and N. Sheppard, Proc. R. Soc. Lond. A 405 (1986) 27.

[16] J.C. Bertolini and B. Tardy, private communication.

[17] J. Silvestre and R. Hoffmann, Langmuir 1 (1985) 621.
[18] D.B. Kang and A.B. Anderson, Surf. Sci. 155 (1985) 639.
[19] A.B. Anderson, D.B. Hang and Y. Kim, J. Am. Chem. Soc. 106 (1984) 6597.
[20] A.B. Anderson and S.J. Choe, J. Phys. Chem. 93 (1989) 6145.
[21] V. Maurice and C. Minot, Langmuir 5 (1989) 734.
[22] R.C. Baetzold, Langmuir 3 (1987) 189.
[23] W.T. Tysoe, G.L. Nyberg and R.M. Lambert, J. Phys. Chem. 88 (1984) 1960.