The catalytic activity of supported platinum: A theoretical study of the activation of H_2

E. Poulain [a,*], V. Bertin [b], S. Castillo [c], A. Cruz [b]

[a] *División Estudios de Posgrado e Investigación, ITTLA, A.P. 750, Tlalnepantla de Baz 54070 Edo., Mexico, Mexico*
[b] *Departamento de Química, CBI, UAM-I. A.P. 55-534, Mexico D.F. 09340, Mexico*
[c] *Area de Física, CBI, UAM-A, Av. San Pablo 180, Mexico D.F. 02200, Mexico*

Abstract

Theoretical calculations, which resemble the supported catalyst, were done for different geometric approaches and electronic states of a platinum dimer interacting with a hydrogen molecule. The $Pt_2 + H_2$ reaction curves have been analyzed and compared with previous platinum monomer plus hydrogen molecule reaction using very carefully theoretical ab-initio methods, including relativistic effective core potential in a multi configuration self consistent field (MC-SCF) and a multi reference configuration interaction (MR-CI) variational and perturbative. From the different H_2 to Pt_2 approaches considered, the parallel one is the most interesting: the A_1 symmetry singlet and triplet states of the system lead to dissociatively capture of H_2. These captures present deep wells, 47 and 30 kcal/mol, respectively, and important activation barriers, 18 and 14 kcal/mol. As a consequence of that, they do not allow easy exit channels; but in the minima of the wells, the Pt–H bond is weak, allowing the hydrogen to participate in catalytic reactions.

Keywords: Platinum; Hydrogen activation; Theoretical calculations

1. Introduction

The hydrogen molecule is a very reactive species — widely employed in experimental catalysis — which is adsorbed dissociatively on most of the clean transition metal surfaces [1]. On the one hand the H_2 chemisorption over metals is used as a tool to determine the free surface metallic area. On the other hand, Pt is the main element used for hydrogenation and dehydrogenation catalytic reactions. So, to study the reaction of Pt clusters with the hydrogen molecule is a subject of real interest.

The H adsorption sites on Pt surfaces are usually observed by studies of high resolution electron energy loss spectroscopy as three folded hollows [2], but also bridged sites are mentioned [1]. The Pt–H bonds are delocalized and preferentially covalent, with small charge transfer. The reported distance and binding energies for the Pt–H bond are very well established and are significant, they go from 1.53 to 1.76 Å [2–4] and the Pt–H binding energies reported go from 56.6 to 60.9 kcal/mol [1].

In the old literature, the chemisorption of H_2 on Pt surfaces was, generally, reported as acti-

* Corresponding author.

vated processes, but these results were obtained mainly over contaminated metallic surfaces. In a recent work it was determined that this process is not activated [5]. Also, by experiment it was suggested that the dissociation of H_2 can be reached when H_2 approaches the metallic surface along its molecular axis and as the polarizability of the H_2 perpendicular to the H–H bond is larger, it is reasonable to expect that the hydrogen molecules will mainly be dissociatively adsorbed with the H–H bond parallel to the metallic surface [5].

Commercial Pt catalysts have high dispersion. In the case of the bifunctional Pt/alumina catalyst, used in reforming petrol processes, dispersions of 95% are reached, i.e. almost the total Pt atoms are in the catalyst surface and particle sizes ≤ 10 Å are the most frequent. These small particles have necessarily anomalous crystalline structures [6], in which, nevertheless, the metallic character of Pt persists, as the Pt–Pt distance [7]. In supported metallic catalysts, the particle size and its geometry are the determining factors of their catalytic properties. By extended X-ray absorption fine structure (EXAFS) were determined, for Pt/alumina and Pt/silica catalysts, Pt–Pt distances of 2.72 Å and 2.76 or 2.775 Å, respectively [7,8]. These values are similar to the reported distances in Pt foils: 2.77 and 2.775 Å [7,8]; the uncertainty in interatomic distances is estimated to be about 0.03 Å. So, the metallic distances in the catalysts are not strongly modified. On the contrary, in the catalysts an important diminishing of the Pt coordination number is observed, compared with the Pt foil: 3.3 or 3.2 and 12, respectively. This fact is interpreted by the authors [7] due to the presence of very small Pt particles, of five metal atoms, in which four of them are in contact with the oxygen of the support. There are some other elements in the surface like chlorine, usually present in the catalyst precursor, it has a Pt coordination number lower than 0.5, falling in the experimental error range, so its influence in the Pt activity may be discarded. These catalysts have a H/Pt ratio of 1.0.

During the thermal oxidative and reductive treatments of the catalysts, looking for a better dispersion and stability of them, there is an evolution of the active centers. EXAFS spectroscopy showed that the Pt nucleation centers may also dissociate the hydrogen molecule. The Pt nucleation process in small particles is related to the support and appears to be a two dimensional growth of the (111) Pt plane [9].

The small size of the catalyst metallic clusters indicates that electronic interactions are very important. As a consequence, theoretical studies appear to be useful and appropriate tools to determine the platinum activity with hydrogen molecules reaction. Few ab-initio studies of the dissociatively adsorption of H_2 by Pt free clusters are available, among them we can mention:

One of the first studies of the Pt–H_2 reaction was published by one of us [10], using the same ab-initio method of this work. We found that the top-on side approach of H_2 to the Pt atom, in the closed-shell excited state $^1A_1$, is the most efficient to capture and dissociate the hydrogen molecule. At the capture of the hydrogen molecule, the H–Pt–H angle is 25.3°, whereas when H–H bond is allowed to relaxed, the angle H–Pt–H was near to 100°. The depth of well was 25 kcal/mol and no activation barrier was found. Whereas, for the $^3A_1$ Pt–H_2 reaction state, which correlates with the platinum ground state, does not present capture of H_2, so, a naked Pt atom in its ground state does not chemisorp H_2. These results are partially reproduced in the linear approach [11], where there is also capture of H_2 by Pt only by a singlet excited $^1A_1$ state, but in contrast, there is no additional gain in energy by the H–H relaxation. In almost all the geometric arrangements of the Pt + H_2 reaction, the triplets showed non-bonding character.

Wang and Pitzer [12], in a previous work, did some studies of the ground and excited states of PtH and PtH$^+$ using ab-initio SCF calculations, with a relativistic effective core potential, being followed by CI calculations. Their bonding energies, bond distances, vibration frequencies and

ionization potentials are in reasonable agreement with experimental results. Between the results reported, they conclude that the 6s and 5d Pt orbital interact strongly with the 1s H orbital.

In 1988 Nakatsuji et al. [13] presented a study of the $Ptn + H_2$ reaction ($n = 1, 2, 3$), using symmetry adapted cluster (SAC) and SAC-CI methods. They also found, as Poulain did, that a single Pt atom breaks the H–H bond, without any barrier, in an active Pt excited state $^1S(d^{10})$ and also, that the Pt $^3D(d^9s^1)$ ground state is not active. When spin–orbit coupling corrections were included, they obtained essentially the same results. For the bonded Pt_2H_2 system they also found a singlet A_1 state as the lowest. Both results are in agreement with the previous mentioned work. In addition, they suggested that the Pt_2H_2 complex is not a good model for the chemisorption of H_2, while on the contrary, PtH_2 and Pt_3H_2 are better models for the dissociatively H_2 capture, because in the $Pt_2 + H_2$ reaction they found an important activation barrier of 28 kcal/mol, which is not present in the other two cases. These authors report 12 kcal/mol for the $Pt_2 + H_2$ reaction well. For bigger clusters, they found that a linear structure of Pt_3, in a parallel asymmetric H_2 approach, efficiently dissociate the hydrogen molecule, but the triangular structure of Pt_3 with H_2 approaching parallel to a side of the triangle was more effective. As Wang and Pitzer, they found that the 5d orbitals of Pt are important in the H_2 dissociation.

A most recent series of studies was made by Balasubramanian with a complete active space (CAS) MC-SCF method, followed by MR singles + doubles CI [14–16]. Their results for the PtH_2 [14] system are like the previous cited calculations. For Pt_2H_2 [15] the author considers four different geometric approaches, only the singlet states are developed. The lowest $^1A_1$ excited state was the most reactive species and the best approach was the parallel. When they included the spin–orbit coupling, they found that the effect is significantly larger (26.7

kcal/mol) for the $Pt + H_2$ dissociation limit than for the system stabilization well (2.8 kcal/mol). In other words, the spin–orbit coupling is not very important when the reaction is accomplishing. This author reports 31 kcal/mol for the depth of the well, 21 kcal/mol for the activation barrier, 2.85 a.u. for the $Pt_2 – H_2$ distance and a broken H–H bond distance of 4.9 a.u. [15].

In this work we present a complete ab-initio quantum chemical MO study of a Pt_2 cluster interacting with a single H_2 molecule with a very deep discussion on the catalytic importance. We present and compare singlet and triplet states in several different geometric approaches. The triplet states are reported here for the first time.

2. Method of calculation

The calculations of the Pt_2H_2 reactions were made with the ab-initio HF-SCF using a relativistic pseudopotential to represent the core-valence electronic interaction of the Pt atoms. The correlation effects are considered by MC-SCF followed by extended MR-CI, variational and perturbative, with the CIPSI algorithm [1] [17]. The method used has been described elsewhere [10,11].

The atomic basis functions for the Pt valence electrons are Gaussian type (3s1p4d//2s1p3d) developed by Durand and Barthelat [18] including a p-polarization function. The relativistic effective core potential of Pt is due to Barthelat et al. [19]. The H basis set is the one reported by Van Duijneveldt [20] (4s2p/2s2p) including two p-polarization functions. The p-polarization functions were made following the Clementi recipe [21].

The reliability and quality of the method used is demonstrated by the agreement between our

description of the singlet states of the PtH_2 and Pt_2H_2 complexes [10,22] and equivalent reported studies [13,15]. In the Pt–H species the differences with experimental results are 1% for the Pt–H distance, 20% for the dissociation energy and 2.8% for the vibration frequency [4]. The calculated and the experimental split between the Pt $^3D(d^9s^1)$ and Pt $^1S(d^{10})$ states differs 0.26 kcal/mol.

The method followed was done with a restricted geometric optimization, without using analytical gradients. With the H–H distance bond fix at the free molecule value (0.7 Å), we calculated a series of points of the potential energy curve, moving the H_2 molecule, from a long distance to the Pt_2 cluster, searching for the minima. The Pt–Pt distance is the reported equilibrium value for catalysts (2.77 Å). If capture was found, the H–H distance was relaxed and optimized at each point until getting a new

potential energy curve. The Pt–Pt distance was not optimized because we are not considering reconstruction effects of the surface catalyst particle. In all the cases Hartree Fock (HF) SCF + MC–SCF + MR–CI were used in each point of the calculated pathways. Several geometries of H_2 approach to Pt_2 were considered, including the parallel, the collinear and two different perpendicular approaches, the first one with a Pt atom interacting with the two H atoms and the other with one H atom interacting with the two Pt atoms (Fig. 1). Thus, the calculations were achieved in the C2v symmetry and we explored singlet and triplet states of its symmetry representations.

3. Results

We organize the results according to the geometry of the approach.

3.1. Parallel approach in Pt_2H_2

Of the different approaches considered between the fragments, the parallel was the most favorable to the capture and scission of H_2. We mentioned above that, in accord with experimental reports, it is reasonable to expect that the hydrogen molecules will be dissociatively adsorbed with the H–H bond parallel to the metallic surface [5].

The most stable Pt_2H_2 states are the $^1A_1$ open shell and the $^3A_1$ states. In both cases the H_2 molecule was captured and completely dissociated. The minima are separated 17 kcal/mol, with the ground state being the singlet. But, in the free fragments there is an inversion: the lowest singlet state is located 3 kcal/mol over the triplet ground state. In other words, the $Pt_2 + H_2$ separated species ground state is a triplet, but the ground state of the joined Pt_2H_2 system is a singlet.

3.1.1. Singlets
The two lowest $^1A_1$ states are connected by an avoided crossing resulting in a deep well, the
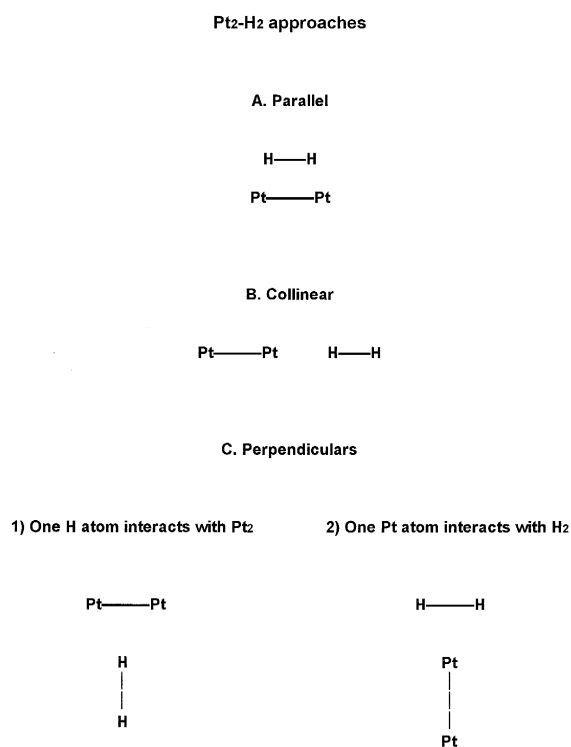

Fig. 1. The hydrogen molecule to platinum dimer geometrical approaches considered in this work. Both singlet and triplet states studies are included for each geometry.

lowest being an open shell system and the upper the closed shell state. The potential energy curve of these $^1A_1$ states were first studied for fixed H–H bond, as a function of the distance between the H_2 and Pt_2. When we studied the ground singlet state alone, we found a completely repulsive curve, but if we made simultaneously the study of the two A_1 lowest singlets, we obtained the correct behavior of the system.

In Fig. 2 we present the potential energy curves for these two lowest singlet states of the A_1 symmetry, when H_2 is approaching parallel to the Pt dimer. In these reaction curves the H–H distance was optimized at each step of the calculation. The upper curve is correlated, at large Pt_2–H_2 distance, with an excited Pt_2^* which is formed by two Pt $(5d^{10}6s^0)$, so it corresponds to the excited singlet state of Pt_2H_2 $(^1\Sigma_g)$. The lowest curve correlate with Pt_2 $(^1\Pi_u)$ + H_2, where the dimer is formed by two Pt $(5d^9 6s^1)$ and corresponds to the ground singlet state of Pt_2H_2. The excited singlet state of the Pt_2^* + H_2 separate fragments (upper curve) is located 37 kcal/mol over the lowest singlet $Pt_2 + H_2$ dissociation limit. The open and closed shell singlet curves met in an avoided crossing originating the deep well and the important barrier observed in the lowest singlet state, as well as the less deep well in the excited singlet state. The lowest minimum has a depth of 47 kcal/mol, with respect to the zero energy, the corresponding Pt_2–H_2 distance is 2.8 a.u. and the H–H distance has a very relaxed value of 4.5 a.u. which, compared with the free H_2 molecule bond of 1.41 a.u., represents an H–H bond rupture, in spite of the presence of an activation barrier of 14 kcal/mol. The other minimum is very near the crossing, i.e. at a Pt_2–H_2 distance of 3.8 a.u. and the minimum is found at 23 kcal/mol under its separate fragments level.

In the region of the energy stabilization there is a significant contribution of the Pt $(5d^9 6s^1)$ configuration in each Pt center, while, far out-
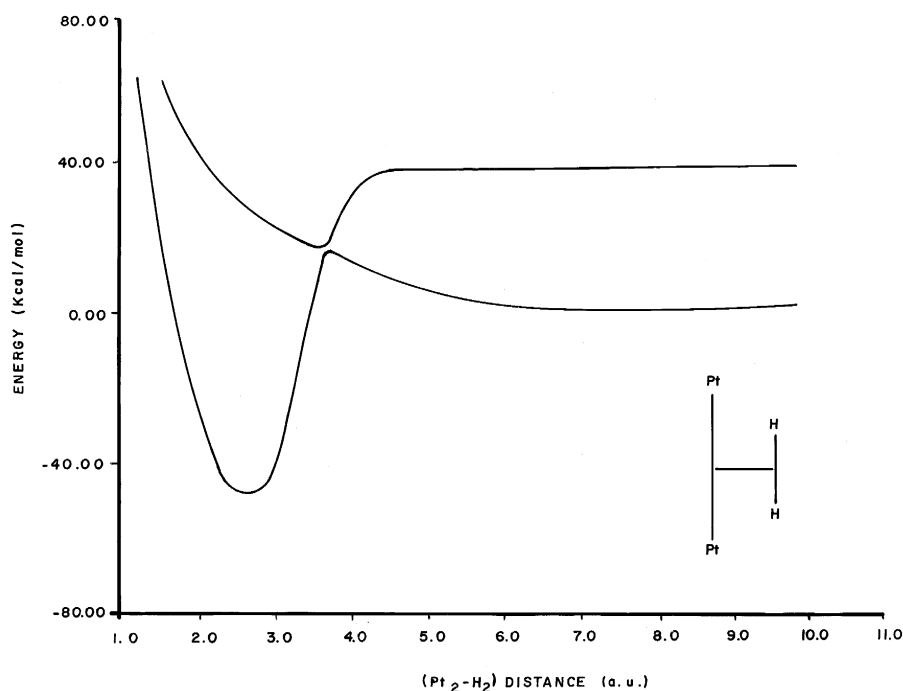

Fig. 2. Potential energy curves for the Pt_2 H_2 reaction in the parallel geometry for the two lowest singlet states of the A_1 symmetry. These curves correspond to the optimized relaxed process of the H–H bond. The upper curve corresponds to an excited closed shell state, the lowest one correspond to the open singlet which correlate with the Pt_2 $(^1\Sigma_g)$ + H_2 free fragments.

side of the minimum, the predominant configuration is a Pt $(5d^{10}6s^0)$. The change of configuration for the $^1A_1$ more stable state of Fig. 2, is a consequence of the avoided crossing since the crossing necessarily mixes the configuration curves of the upper Pt $(5d^{10}6s^0)2 + H_2$ with the lowest Pt $(5d^96s^1)_2 + H_2$.

The capture of H_2 by the Pt dimer, once it occurs, has no exit channel since the captured H atoms need 61 kcal/mol to reform the H_2 molecule (47 kcal/mol for the well and 14 kcal/mol for the barrier).

So, from the lowest singlet state of Pt_2H_2 we can reach the dissociatively capture of H_2, if the barrier is surpassed. Another possibility can arise by excitation to the first excited singlet state of Pt_2 when interacting with H_2, and then, allow a softly decay of the Pt_2H_2 complex to the ground state, via the avoided crossing. Unfortunately, there is no experimental evidence of this possibility.

The Pt_2H_2 considered is a *cis* geometry, we do not make any calculation of the *trans* isomer because we are considering the case of a supported Pt_2 particle and H is not stably dissolved in Pt crystals [5]. Moreover, as was mentioned above, it is possible for H_2 to be chemisorped parallel to the Pt surface in the catalysts [5]. Other authors [15], found that the *trans*-isomer is the global minimum of the potential energy for the naked $Pt_2 + H_2$ system, which is not important for supported catalysts.

Our results, together with other reports, are presented in Table 1. All the theoretical values are, in general, similar to ours. Since the authors of Ref. [13] do not report capture, nor activation of the H–H bond, they do not report the Pt_2–H_2 and the H–H distances. As we can see, all the theoretical heats of adsorption (or depth of wells) are overvalued, with the exception of the Nakatsuji et al. report. With this values we calculated the binding energies as the semi sum of the depth of the well and the dissociation energy of H_2 (103.25 kcal/mol), obtaining, than our case, 75 kcal/mol for the singlet and 66.5 kcal/mol for the triplet. The experimental value is ~ 60 kcal/mol [1], i.e. the differences are ~ 25 and 11%. Our Pt–H dissociation energy, obtained previously [10], was around 80% of the empirical estimation [4]. Experimentally the chemisorption of H_2 on Pt surfaces is non-activated [5], i.e, no barrier was detected. In all the theoretical calculations of the capture of H_2 by the Pt dimer presents big barriers. It is possible that the active site is not necessarily the dimer, or, the process occurs from an excited state. Actually, we are performing calculations on Pt_3H_2 with the purpose to elucidate this discordance.

It is also illustrative to compare the above results for the Pt_2–H_2 reaction with our previous results for the reaction of a single Pt with an H_2 molecule (Table 1). Both PtH_2 and PtH_2 systems capture and rupture the H_2 molecule in

Table 1
Energies and geometric parameters of the Pt_2H_2 reaction. Comparison with other reports

Species	Type of approach	State	Depth of well	Pt–H distance	H–H distance	Activation barrier	Ref.
PtH$_2$	on top	$^1A_1$	25	2.75	3.3	0.0	[10]
PtH$_2$	on top	$^3A_1$	0.0	no capture	—	—	[10]
Pt$_2$H$_2$	parallel	$^1A_1$	47	2.8	4.5	14	this work
Pt$_2$H$_2$	parallel	$^3A_1$	30	2.8	5.5	18	this work
Pt$_2$H$_2$	parallel	$^1A_1$	12	not reported	not reported	28	[13]
Pt$_2$H$_2$	parallel	$^1A_1$	31	2.85	4.9	21	[15]
Pt crystal Experim.	suggested parallel		10–18[b]	2.89–3.33	—	0.0	Experim. [1,5]

All energies in kcal/mol. All distances in a.u.
[a]According to the cluster this distance is Pt–H_2.
[b]Equivalent to the heat of adsorption.

singlet closed shell states. Also, both of them present avoided crossings with other excited open shell singlets, which originate the deep wells in the lowest states. The PtH_2 system stabilizes under the initial free fragments in its ground state (the triplet) with an energy of 25 kcal/mol. The stabilization is greater for Pt_2H_2, 47 kcal/mol, measured from the ground $Pt_2 + H_2$ state, which is also a triplet state. This greater stabilization shows the effect of reinforcement of the second Pt atom in this type of collision. We will see that the second Pt atom in other configurations poison the activity of the Pt atom placed near the hydrogen molecule. As it was mentioned before, experimental works suggested that the capture of H_2 occurs with the H–H bond parallel to the Pt surface, not with a Pt atom located in a step of the crystal, also the experiments show a ratio Pt/H = 1/1. So, there is better agreement of both experimental evidence when we consider Pt_2H_2 instead of PtH_2. But the experimental value of the well is lower than ours: 10–18 kcal/mol [1], showing the

possible influence of more Pt atoms. For the Pt monomer, in the capture of H_2, the H–Pt–H angle is 25.3° and in the minimum of the curve is nearly 100°, indicating clearly the bond scission. In this minimum the Pt–H distance is 2.75 a.u. and for the case when the H–H is at its equilibrium distance, was 3.28 a.u. For the Pt dimer the capture is presented at 2.3 a.u. and the minimum of the relaxed system occurs at 2.8 a.u. The corresponding experimental value is reported, as was mentioned above, between 2.89 and 3.33 a.u., values more similar to the $Pt_2 + H_2$ result. The relaxed H–H distance for Pt_2H_2 is greater than for PtH_2: 4.5 and 2.62, respectively, so in Pt_2H_2 each H is located almost over a Pt atom. But contrary to most of the other transition metal cases, where the highest symmetry is a determinant factor in the stability, this system is not collinear. The experiments show that H_2 is not absorbed on the platinum catalyst which is completely in agreement with this last theoretical result.
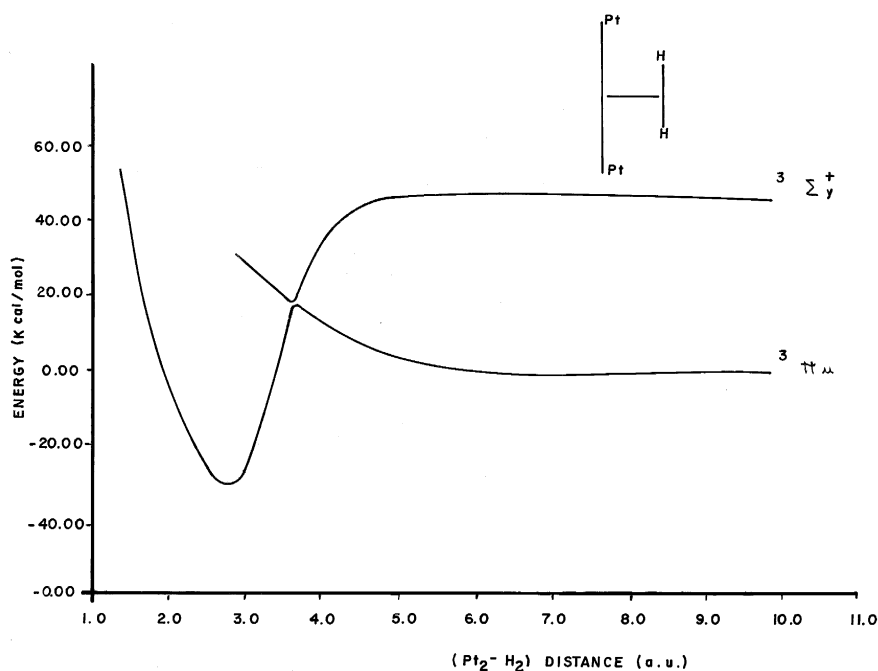
One of the more striking conclusions of our

Fig. 3. The potential energy curves for the Pt_2H_2 interaction, in a parallel mode, of the two lowest triplet states of the A_1 symmetry. It corresponds to the optimization of the relaxation process of the H–H bond. The zero energy is taken to the Pt_2 and H_2 free fragments in their ground state.

previous work was that a Pt atom in its $^3D(d^9s^1)$ ground state does not capture nor activate the H–H bond, only there is a minimum for the linear symmetric case, but is not reachable due to a great activation barrier [11]. On the contrary, the Pt_2 dimer in triplet excited state captures and activates the H_2 molecule and then through an avoided crossing dips down to reach the potential energy curve of the lowest triplet state.

3.1.2. Triplets

In the approach of H_2 to the Pt dimer, with a fixed H–H distance of 1.41 a.u., the potential energy curve of the A_1 triplet is striking similar to those of the A_1 singlet. From the shape of this curve it is clear that it is necessary to include other excited states. The next triplet state of the free fragments is located at 46 kcal/mol over the zero level.

As was the case for the singlet A_1 states, these two lowest A_1 triplets present an avoided crossing.

In the relaxation of the H–H bond appear two minima, one at the Pt_2–H_2 distance of 2.8 and the other at 3.6 a.u. The avoided crossing is located close to the second minimum, as seen in Fig. 3. The lowest curve in this figure corresponds to the reaction $Pt_2 + H_2$ with Pt_2 in its ground state, which has a big contribution of the Pt $(5d^96s^1)$ configuration. In the deep well the Pt_2–H_2 distance is 2.8 a.u. and its relative energy is 30 kcal/mol below the energy of the free fragments in the ground state. The relaxed H–H distance in this minimum is 5.5 a.u., showing the total rupture of the bond. For this state in the Pt_2–H_2 approach there is also a barrier of 18 kcal/mol To our knowledge, these are the first results reported for the triplet behavior of the Pt_2H_2 system.

As mentioned above, in experimental works, platinum is the main metal used to prepare hydrogenation catalysts. Our theoretical study shows that one reason is that the Pt has multiple channels of reaction with H_2, and the other is that the capture and the activation of the H_2

molecule happens in a great diversity of geometries and electronic configurations, both for the monomer and for the dimer. In the last case in singlet and triplet states. It is difficult to find in the literature other transition metals with this variety of characteristics, i.e. nickel, a widely theoretically studied metal [23].

The triplets, as the singlets, can reach the capture and activation of the H_2 molecule by first exciting the Pt dimer in interaction with the H_2 molecule and then decaying softly to the rupture state through the avoided crossing.

In comparing the characteristics of the triplet and singlet A_1 curves in the region of the minimum, we find that the stabilization of Pt_2H_2 occurs for the same Pt_2–H_2 distance, but the H–H distance is larger for the former system (5.5 and 4.5, respectively); the barrier is greater (18 and 14 kcal/mol, respectively) and the depth of the well is lower (30 kcal/mol) for the triplet than for the singlet (47 kcal/mol). So, once the capture is attained, it is necessary to provide 48 kcal/mol to induce the inverse reaction, 13 kcal/mol less than for the singlet. Looking to other metals we find for instance the $Cu + H_2$ reaction, which is completely reversible [24]. In conclusion, the Pt_2 triplet state performs very similarly to the singlet state with the H_2 molecule, with the advantage that in this case we start in the ground state of $Pt_2 + H_2$.

3.2. Collinear approach in Pt_2H_2

We began our study of this geometry configuration keeping the H–H distance fixed at 1.41 a.u.; there is a weak capture, in a $^1A_1$ state, of the H_2 molecule at a Pt_2–H_2 distance of 3.3 a.u. with bond energy of less than 8 kcal/mol. The relaxation of the H–H distance raises the energy notably, without any minimum. Balasubramanian [15] found almost the same result, but in his study, he considered different potential curves increasing the H–H distance from 0.76 to 8.0 Å, being the lowest curves (Fig. 5 of this reference) almost without well. The potential energy curves for successive increasing of the
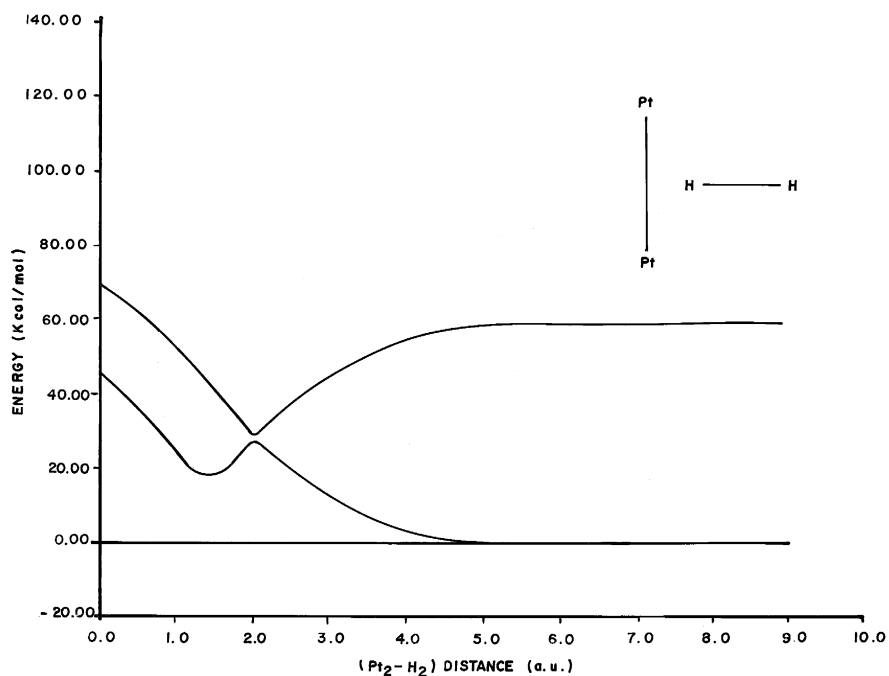
Fig. 4. The Pt_2H_2 interaction energy curves of the relaxation process of the H–H bond for the two lowest singlet states of the A_1 symmetry, in the perpendicular geometry where one H atom interacts with Pt_2. The zero energy is the same used for the other curves.
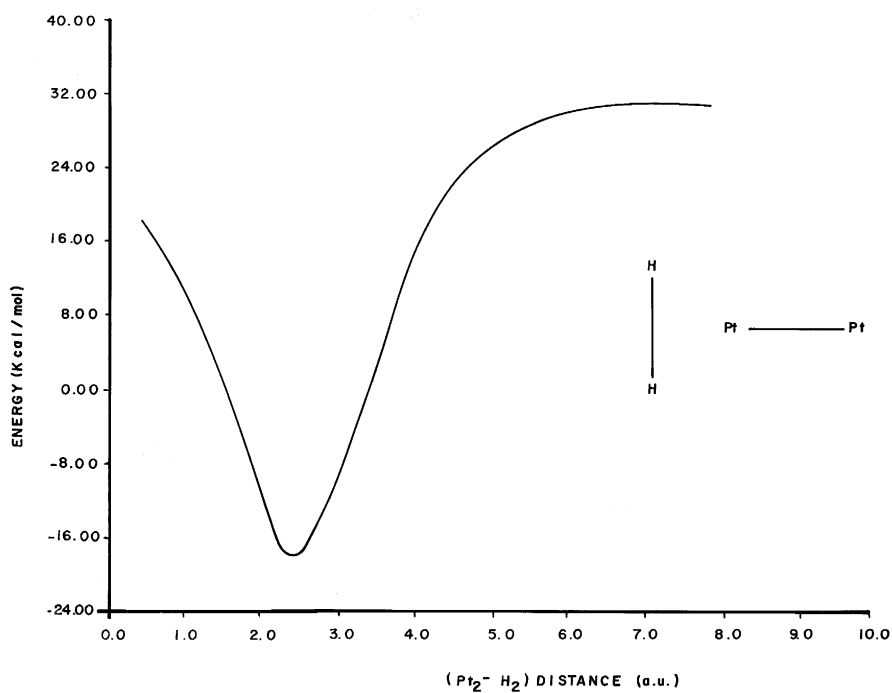

Fig. 5. The potential energy curve for the Pt_2H_2 interaction of the relaxation process of the H–H bond for the lowest singlet state of the A_1 symmetry, in the perpendicular geometry, where one Pt atom interacts with H_2. The zero energy is the same as used for the other curves.

H–H distance became higher in energy and the depth of the wells is larger. The deepest well is found for a H–H distance of 8.0 Å, where the Pt_2H_2 species became Pt–Pt–H + H, a result obtained first by Gavezzotti et al. [25].

The collinear approach in the $^3A_1$ state is also a non-favorable configuration for the H_2 scission capture. In this potential energy curve the H–H distance is maintained at the equilibrium value and the well is not so deep as that in the $^1A_1$ state; there is a weak capture of the H_2 molecule at a Pt_2–H_2 distance of 3.2 a.u., but the energy of the well depth is almost of the size of the calculation error.

We may conclude that this geometry only captures the hydrogen molecule very weakly and does not activate the H–H bond. In experiments the hydrogen molecules collision with the catalyst surface in any geometric approach, then, they may be captured in the collinear one, due to the fact that the rotational energy of the H_2 molecule is very small, and that the molecule has big possibilities to be activated in other geometry's.

3.3. Perpendicular approaches in Pt_2H_2

3.3.1. One H atom interacts with Pt_2

The potential energy curves of the two lowest $^1A_1$ states in this approach, with the H–H distance optimized, is presented in Fig. 4. We obtain again an avoided crossing for a H_2–Pt_2 mass center distance of 2 a.u., resulting in two minima, the lowest occurs at 1.3 a.u. and it is located at 18 kcal/mol over the energy of the free singlet fragments. There is a great barrier of 26 kcal/mol before the well. In Ref. [15] this barrier is 37 kcal/mol for the same H–H distance and it is strongly diminished when the H–H distance is relaxed but in this case we have in reality Pt–Pt–H + H, which is again a known result.

The potential energy curve of the $^3A_1$ state of this same approach, with fixed H–H distance is very similar to the previous triplet presented, there is a very weak capture at a Pt_2–H_2 dis-

tance of 5.5 a.u. with an energy of few kcal/mol also of the size of the calculation error. The relaxation of the H–H bond do not contributed to the capture, neither the dissociation of the H–H bond.

Our conclusion is that the capture of the H_2 molecule on the Pt surface may occur in the same way as in the previous geometric approach. It is important to notice that in this case and in the previous geometry one, there are captures of the H_2, weak in both cases but it is capture, which allow us to ensure that any rotation of hydrogen molecule may induce the activation of the hydrogen bond.

3.3.2. One Pt atom interacts with H_2

This geometric approach resembles the PtH_2 system but we must consider the effect of the second Pt atom over the activity of the Pt atom interacting with the H_2 molecule. The potential energy of the $^1A_1$ state presents an attractive character for a H–H distance fixed at 1.41 a.u. The relative minimum is located at a Pt- mass center of H_2 distance of 3.0 a.u., with a H–Pt–H angle of 26.5° and the stabilization energy of 4 kcal/mol with respect to the energy of the free fragments in their ground state. The free fragments of this $^1A_1$ state are located at 31 kcal/mol over the free fragments in its ground state.

Beginning with the H–Pt–H angle at 27°, in the lowest $^1A_1$ state, when the H–H bond is relaxed the system reaches a new stable geometry with an opened angle of 58.5°, which corresponds to a H–H distance of 2.8 a.u., a Pt–H distance of 2.8 a.u. and a new deep well of 23 kcal/mol measured from the free reactants in its ground state. This H–H optimized distance is almost twice that of the non-relaxed bond, so we can state that the H_2 molecule is dissociated for this geometry case. If we compare this case with the PtH_2 case we find that the state is an excited one, as it is in the monomer, no barriers are present in both cases, the depth of the well is somewhat lower and the H–Pt–H angle is also lower than the monomer, so the H–H

scission for the dimer is not as effective as it is for the monomer. For this geometry arrangement we may predict that: the presence of a second Pt does not favor the activity of a single Pt atom located in a step of the catalysts.

Another important fact of this case is that there is no initial barrier for the reaction, so the curve goes down very deep to the minimum where the hydrogen bond is very relaxed allowing any secondary reaction, which is the final purpose of Pt catalysts.

4. Charges

Here we discuss briefly the distribution of charges for the lowest $^1A_1$ state of the parallel approach. There is charge transfer, in the region characterized by the closed shell configuration curve (Fig. 2), from the occupied H_2 (1σ) molecular orbital (m.o.) to the empty Pt (6s) atomic orbital (a.o.) and from the occupied Pt($5d_{yz}$) a.o. to the empty H_2 $(1\sigma^*)$ m.o. This transfer results in the activation of the H–H bond. On the contrary, in the region of the curve characterized by the open shell predominance there is charge transfer from the Pt_2 to the H_2. If the transfer occurs in the opposite sense, the bond is also activated [15].

The charge at each atom of the most stable Pt_2–H_2 state are reported in Table 2. In the equilibrium region the Mulliken population of each Pt atom is 10.17, of each H atom it is 0.83, these values indicate the mentioned charge transfer. In Table 2 is observed, as was found in Ref. [15], that the Pt (6p) a.o. participation in the Pt charge is small (0.12) and the population favor the $5d^9 6s^1$ configuration for the Pt atom in its ground state.

Table 2
Population analysis of $Pt_2 H_2$ in the ground $^1A_1$ state, at the capture distance of H_2 and in the parallel mode of reaction

	Pt	H	Pt(s)	Pt(d)	Pt(d)	Pt–H
This work	10.17	0.83	0.95	0.12	9.10	0.55
Ref. [15]	9.99	1.01	0.67	0.10	9.20	0.55

5. Conclusions

The most effective configuration for the Pt_2 + H_2 reaction is the parallel geometry, in which singlet and triplet A_1 states clearly break the H–H bond. The ground state of the $Pt_2 H_2$ system is the singlet state. The triplet state is 17 kcal/mol over the singlet and presents a very similar behavior, compared with the monomer which is only active in the singlet state. The activity of the $^3A_1$ state of the dimer is reported here for the first time.

The Pt dimer singlet and triplet A_1 states give raise to deep wells, 30 and 47 kcal/mol, more important than for the monomer, 25 kcal/mol. Due to the important activation barriers in the far outside region of the wells, in both spin multiplicity, there are no exit channels for the H atoms, when the capture is reached. This is a notable different behavior compared with the Pt singlet: there is no activation barrier when the hydrogen molecule is approaching. On the other hand, the reactions of the Pt_2 clusters with H_2 present avoided crossings of the potential energy curves, these avoided crossings generate the deep wells and give rise to an alternative mechanism for the dimer reaction.

There is a possible mechanism to activate H_2: it is to excite the Pt cluster to an upper state and from them to reach the upper curve of Fig. 2 or Fig. 3, then softly decaying through the avoided crossing to the minimum, to reach a stable state, but in the minimum the H_2 molecule is broken and the H atoms are bonded weakly to the Pt atoms through H(s)–Pt(d) overlap. This last result explains the reason why the H chemisorped atoms can easily react with other neighboring molecules, which explains the catalytic effect of supported platinum.

From the others geometries considered in $^1A_1$ state, the perpendicular approach is effective in the scission of the H–H bond, in this case the H_2 molecule interacts with one of the Pt atoms, as in a Pt monomer. The study of this mode of approach gives evidence that the second Pt atom acts as a weak poison to the first Pt atom when

the hydrogen molecule approaches. This particular fact may need more attention, because it can provide light in the loss of activity of the Pt catalysts when the particle size is big.

Another important conclusion is that in all the geometrical approaches there is capture, which in most cases is weak, but in all of them is possible to reach the most favorable geometry due to the fact that any small rotation of the hydrogen molecule gives the right position for getting the rupture of the H–H bond.

The great variety of Pt monomer and dimer geometries and spin states presenting capture of hydrogen and the possibility to rupture the H–H bond, explain, in part, the reason to use platinum for hydrogenation catalysts. The future of this study is to clarify if bigger clusters show the same characteristics.

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