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Density Functional Study of Ethylene Adsorption on Palladium Clusters

A. Fahmi* and R. A. van Santen

Schuit Institute of Catalysis, Laboratory of Inorganic Chemistry and Catalysis, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

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Fully optimized geometries and adsorption energies obtained from nonlocal density functional calculations are presented for Pdₙ(C₂H₄) (n = 1–6) clusters. The adsorption mode can be π or di-σ according to the cluster size. The di-σ adsorption mode is characterized by a strong distortion for both the ethylene and the metal cluster. The potential energy surfaces for the C–H activation show that the d¹⁰ configuration of palladium is suitable for the formation of the π molecular complexes, whereas the d⁸s¹ configuration is suitable for the formation of the σ bonds of the vinyl–hydride products.

1. Introduction

In recent years, numerous experimental and theoretical investigations of chemisorption of ethylene on a variety of transition metal surfaces have been carried out utilizing a wide range of techniques. Upon adsorption on a metal surface, ethylene undergoes dehydrogenation—hydrogenation processes that lead to several C₃H₂ species on the surface. Despite various experimental studies, reaction mechanisms leading to these species and their localization on the surface are not well determined.

At low temperature (100 K), ethylene is molecularly adsorbed on the metal surface. Two adsorption modes are often discussed: the di-σ adsorption mode where ethylene interacts with two metal atoms and the π adsorption mode where ethylene interacts with a single metal atom. High-resolution electron energy loss spectroscopy (HREELS) experiments provide vibrational spectra for adsorbed intermediates on the metal surface. The comparison with the spectra of C₂H₄Br₂ (a model for π-bonded C₂H₄), Zeise’s salt (a model for π-bonded C₂H₄), and gaseous C₂H₄ allow Stuve and Madix to introduce a πσ parameter to characterize the adsorption of C₂H₄. The πσ parameter is zero for gaseous C₂H₄ and unity for C₂H₅Br₂. For adsorbed ethylene, the πσ parameters for Pd(100), Pd(111), and Pd(110) surfaces are 0.78, 0.43, and 0.39, respectively. These values are attributed to the formation of a di-σ complex on Pd(100) and a π complex on Pd(111) and Pd(110) surfaces. Extended Hückel calculations have shown that the adsorption mode of ethylene is controlled by a subtle balance between attractive two-electron interactions and repulsive four-electron ones (the Pauli repulsion).

Ethylene behaves differently in the two adsorption modes. At 80 K, the two modes coexist on the Pd(100) surface. While the π-bonded ethylene desorbs upon heating from 100 to 300 K, the di-σ-bonded ethylene dehydrogenates into coadsorbed atomic hydrogen and vinyl species. The difference in reactivity should be related to the difference in geometry and electronic structure of ethylene in the two adsorption modes.

In this work, we present a density functional study of the interaction of ethylene with palladium. Clusters of 1–6 metal atoms are used. The two adsorbed ethylene species π and di-σ are described. The activation of the C–H bond of ethylene is analyzed for the single atom and the dimer. One of the main aspects of our calculations is a full geometry optimization of the whole system C₂H₄/Pdₙ. This approach is different from the common approach that consists in freezing the cluster, which is supposed to simulate a metal surface and optimizing the adsorbate. On one hand our approach will give information about the magnitude of the local relaxation induced by the adsorption of ethylene on the palladium surface. On the other hand, our calculations should describe the interaction of ethylene with palladium clusters in the gas phase. The calculation method is described in section 2. The molecular properties of the bare Pdₙ clusters are presented in section 3. Adsorption and activation of the C–H bond by the palladium single atom and dimer are discussed in sections 4 and 5, respectively. Section 6 is devoted to the evolution of the ethylene adsorption with the cluster size.

2. Method of Calculation

A density functional method is used to determine geometries, adsorption energies, and transition states for the C₂H₄/Pdₙ (n = 1–6) systems. We have performed quasi-relativistic spin-unrestricted, frozen-core calculations using the Amsterdam Density Functional (ADF) program. The program represents the molecular orbitals as linear combinations of atomic Slater-type orbitals and solves the Khon–Sham one-electron equations using the Vosko–Wilk–Nusair local spin density approximation (LDA). To correct the overbinding inherent to LDA, nonlocal gradient corrections for the exchange (Becke functional) and correlation (Perdew functional) terms were computed self-consistently. Relativistic effects were taken into account by first-order perturbation theory. For the carbon atom, a frozen core potential is used for the 1s electrons; for the palladium atom, electrons up to the 4p shell are frozen. The basis sets are of double-ζ quality except the palladium d orbitals which are triple-ζ.

Adsorption energies have been calculated according to the expression:

\[ E_{ads} = E_{(C₄H₄/Pdₙ)} - (E_{Pdₙ} + E_{C₄H₄}) \]

where \( E_{Pdₙ} \) and \( E_{C₄H₄} \) are total energies of the bare cluster and ethylene, respectively, and \( E_{(C₄H₄/Pdₙ)} \) is the total energy of the adsorbate/substrate system. A negative \( E_{ads} \) value corresponds to a stable adsorbate/substrate system.

3. Bare Pdₙ (n = 1–6) Clusters

3.1. The Palladium Single Atom. As a reference point, we have calculated the splitting between the two lowest states.
of the palladium single atom. The calculated energy difference between the $1S(d^{10})$ ground state and the $3D(d^8s^1)$ excited state is 26 kcal/mol; the experimental value is 22 kcal/mol.\(^\text{11}\)

3.2. The Palladium Dimer. In agreement with previous theoretical calculations (Hartree-Fock\(^\text{12}\) and DFT\(^\text{13}\)), we found the ground state of the palladium dimer to be triplet. The calculated molecular properties are summarized in Table 1 for the triplet and the singlet states. Bonding energies are relative to two Pd($d^{10}$) atoms. The triplet state is more stable by 4 kcal/mol. The estimated experimental bonding energy for the dimer is between 16 and 26 kcal/mol\(^\text{14}\) according to the technique of evaluation. The Mulliken population analysis shows that the singlet state is composed of two interacting $d^{10}$ atoms. The Pd–Pd bond length is shorter and the vibrational frequency is higher for the triplet state.

3.3. The Pd$_n$ (n = 3–6) Bare Clusters. For the Pd$_n$ (n = 3–6) bare clusters, only compact structures were investigated. A density functional analysis of the structure of small palladium clusters show that compact structures are more stable than open structures, and states of triplet spin are more stable than states of singlet spin.\(^\text{15}\) Our calculations show that for Pd$_3$, the triangular geometry ($D_{3h}$) is more stable by 29 kcal/mol relative to the linear geometry ($D_{0h}$). For small clusters, the atomic arrangements are controlled by local bonding and orbital overlapping rather than long-range interaction as it is in the bulk structure. Cluster geometries are cluster size dependent and experimental structure determinations often proceed via indirect methods (for instance $N_2$ adsorption for the determination of the structures of Ni$_n$ clusters\(^\text{16}\)). The other investigated geometries are Pd$_4$ ($T_d$), Pd$_6$ ($D_{3h}$), and Pd$_6$ ($O_h$). The calculated properties are shown in Table 2. All these clusters present ground states of spin triplet, previous DFT, or Hartree–Fock studies of Pd$_3$\(^\text{17}\) and Pd$_4$\(^\text{18}\) clusters have shown that these clusters are indeed triplet. The optimized Pd–Pd bond remains close to the bulk value, 2.75 Å.\(^\text{19}\) The Pd–Pd bond strength decreases with the cluster size but is still far from the experimental value, 15 kcal/mol.\(^\text{19}\) The Mulliken populations (for n = 3, 4, 6) show a decrease of the s electrons and increase of the d electrons with the cluster size. The energy band calculation for the palladium bulk structure\(^\text{20}\) gives 0.37 and 9.63 electrons for the valence s and d orbitals, respectively.

4. The Pd(C$_2$H$_4$) Complex

The Pd(C$_2$H$_4$) complex was first synthesized by Ozin and Power\(^\text{21}\) using C$_2$H$_4$/Xe matrices. This complex has also been subject of theoretical investigations. Blomberg et al., using an ab initio Hartree–Fock method, calculated the bonding energy of the complex\(^\text{22}\) and the activation of the C–H bond of ethylene by the palladium single atom.\(^\text{23}\)

During the interaction of ethylene with a transition metal donation and back-donation processes take place. The donation involves a transfer of electrons from the ethylene π orbital to the metal unoccupied orbitals, whereas the back-donation populates the ethylene π* orbital with electrons from the occupied metal orbitals. This is the well-known Dewar–Chatt–Duncanson mechanism.\(^\text{24}\) Both donation and back-donation are attractive interactions. The repulsion (Pauli repulsion) is due to the interaction between the occupied orbitals of ethylene and the transition metal. The first consequence of the donation and back-donation processes is the weakening of the C–C bond strength, the bond length increases from 1.34 Å in the gas phase to 1.40 Å in the complex. The formation of the Pd–C bonds induces a small rehybridization of the carbon atom from sp$^2$ toward sp$^3$ (see Table 3). The dihedral angle between the HCC plane and the CCPd plane increases from 90° to 98°; for a complete sp$^3$ hybridization, this angle should be 120°. The ground state of the complex is singlet with a bonding energy of −39 kcal/mol. This value is close to that calculated by Blomberg et al.,\(^\text{22}\) −31 kcal/mol. The overall charge transfer is a back-donation of 0.07 electrons to ethylene. The donation to the metal is small, 0.01 electrons.

The potential energy surface for the activation of the C–H bond of ethylene by the palladium single atom (a) and dimer (b); the reference for adsorption energies (in kcal/mol) corresponds to free molecules (Pd + C$_2$H$_4$ or Pd$_2$ + C$_2$H$_4$) in their equilibrium geometries. For the transition states the barrier heights (relative to π and di-σ adsorption for Pd and Pd$_2$, respectively) are indicated. TS1, TS2, and TS3 for Pd$_2$C$_2$H$_4$ correspond to the side-on parallel, side-on perpendicular, and end-on approaches (see Figure 3).

### Table 1: Molecular Properties for the Triplet and Singlet States of the Palladium Dimer

<table>
<thead>
<tr>
<th>Pd$_2$ state</th>
<th>binding energy (kcal/mol)</th>
<th>Pd–Pd frequency (cm$^{-1}$)</th>
<th>Mulliken populations: s/p/d</th>
</tr>
</thead>
<tbody>
<tr>
<td>triplet</td>
<td>−29</td>
<td>2.56</td>
<td>213</td>
</tr>
<tr>
<td>singlet</td>
<td>−25</td>
<td>2.74</td>
<td>187</td>
</tr>
</tbody>
</table>

### Table 2: Molecular Properties of the Pd$_n$ Bare Clusters

<table>
<thead>
<tr>
<th>Pd$_n$ atomic coordination</th>
<th>Mulliken populations: s/p/d</th>
<th>Pd–Pd (Å)</th>
<th>Pd–Pd bond strength (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0/0/10</td>
<td>2.56</td>
<td>29.2</td>
</tr>
<tr>
<td>2</td>
<td>0.55/0.02/9.43</td>
<td>2.76</td>
<td>27.2</td>
</tr>
<tr>
<td>3 $D_{3h}$</td>
<td>0.66/0.03/9.31</td>
<td>2.75</td>
<td>26.2</td>
</tr>
<tr>
<td>4 $T_d$</td>
<td>0.54/0.04/9.42</td>
<td>2.79</td>
<td>23.9</td>
</tr>
<tr>
<td>5 $D_{3h}$ (top)</td>
<td>0.42/0.04/9.56</td>
<td>2.78</td>
<td>23.6</td>
</tr>
<tr>
<td>4 (base)</td>
<td>0.52/0.04/9.42</td>
<td>2.78</td>
<td>23.6</td>
</tr>
<tr>
<td>6 $O_h$</td>
<td>0.46/0.04/9.50</td>
<td>2.78</td>
<td>23.6</td>
</tr>
</tbody>
</table>

### Table 3: Adsorption Energies (kcal/mol) Relative to Free Species and Geometries (Å and deg) for the Molecular Complex, the Transition State, and the Vinyl–Hydride Product of the Pd(C$_2$H$_4$)$_2$ Complex

<table>
<thead>
<tr>
<th>$E_{ads}$</th>
<th>transition state</th>
<th>H–Pd–C$_2$H$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C–C$</td>
<td>1.40</td>
<td>1.32</td>
</tr>
<tr>
<td>Pd–C</td>
<td>2.20</td>
<td>2.00</td>
</tr>
<tr>
<td>Pd–H</td>
<td>2.72</td>
<td>1.68</td>
</tr>
<tr>
<td>H–Pd–C</td>
<td>106</td>
<td>54</td>
</tr>
</tbody>
</table>

*For the transition state, the barrier height relative to the π complex is 36 kcal/mol.
difference between the transition state and the vinyl−hydride product is small, 6 kcal/mol. Our results are in good agreement with Siegbahn et al., calculations, which found a barrier height of 31 kcal/mol and an energy difference of 3 kcal/mol between the transition state and the vinyl hydride product.  

5. Interaction of Ethylene with the Palladium Dimer  

Two kind of complexes can be formed (Figure 2, parts a and b): π and di-σ complexes. The molecular properties of the two complexes are presented in Table 4. The di-σ complex is more stable and is characterized by a large charge transfer from the dimer to ethylene (back-donation). The di-σ adsorption mode gives a strong interaction and a small distortion. The same trend was found by Extended Huckel calculations for the adsorption of C_2H_4 on Pd(111) and Pt(111) surfaces. Table 4 also shows the decomposition of the interaction energy of ethylene with the dimer. The interaction energy is decomposed in three contributions: the Pauli repulsion ΔE_p, the electrostatic interaction ΔE_el, and the orbital interaction ΔE_orb. The Pauli repulsion arises from the interaction between occupied orbitals of C_2H_4 and Pd_d; the electrostatic interaction corresponds to the interpenetrating charge distributions; and the orbital interaction represents the energy change upon the formation of the molecular orbitals of the C_2H_4/Pd_d system. This energy calculated with the Ziegler transition-state method for the optimized adsorbate/substrate system corresponds to the interaction between two distorted fragments and is not the adsorption energy that refers to free molecules in their equilibrium geometries (the sum ΔE_p + ΔE_el + ΔE_orb is not equal to E_ads). The Pauli repulsion is stronger for the di-σ adsorption. However, the compensation by the other contributions is large enough to favor the di-σ adsorption mode.  

We have also analyzed the activation of the C−H bond of ethylene by the palladium dimer. Three structures for the vinyl−hydride product (H−Pd_d−C_2H_3) were investigated: the pseudo-square planar structure (Figure 2c, the vinyl plane is perpendicular to the plane containing the two Pd atoms and the hydrogen atom), the trans (Figure 2d) and the cis (Figure 2e) structures. The optimized parameters are given in Table 5. The square structure is the most stable structure, therefore the vinyl−hydride H−Pd_d−C_2H_3 presents a square geometry equivalent to that of H−Pd_d−CH_3 resulting from CH_4 activation. On the other hand, because of the steric repulsion, the cis structure is less stable than the trans structure by 4 kcal/mol.  

The potential energy surface for the activation of the C−H bond by the palladium dimer is presented in Figure 1 together with that of the single atom. The comparison of the stability of the π complexes and vinyl−hydride products of PD_C_2H_2 and PD_C_2H_4 (see Figure 1) shows that the d^{10} configuration (the palladium single atom) is optimal for the formation of the π complex, whereas the d^{8}s^{1} configuration (that of Pd_d is d^{8}s^{0.55}) should be optimal for the formation of the σ-bonds of the vinyl−hydride product. Indeed, the PD_C_2H_2 π-complex is stable by 39 kcal/mol relative to free molecules in their ground states, whereas the PD_C_2H_4 π-complex is stable only by 23 kcal/mol. On the other hand, the vinyl−hydride H−Pd−C_2H_3 is stable only by 6 kcal/mol, whereas H−Pd_d−C_2H_4 is stable by 38 kcal/mol.  

Three transition states were investigated (Figure 3). In the end-on approach (TS3), the Pd−Pd axis is perpendicular to the C−H bond and only one Pd atom is involved in the interaction. The other Pd atom is kept far from ethylene. In the side-on perpendicular approach (TS2), the two molecules are parallel and the Pd−Pd axis is kept perpendicular to the C−H bond. For the side-on parallel approach (TS1), the Pd−Pd axis is kept parallel to the C−H bond. When only one Pd atom of the dimer activates the C−H bond (TS3), the calculated barrier relative to π adsorption is very close to that of the single atom (37 vs 36 kcal/mol). The barrier relative to di-σ adsorption is larger, 60 kcal/mol, and is a consequence of the energy difference between π and di-σ adsorption modes. The side-on perpendicular approach was found for the activation of N_2  and CH_4 by Pd_d. The transition state (TS2) is characterized by a long Pd−Pd distance (2.92 Å). While the vinyl group is attached to the two Pd atoms, the hydrogen atom is attached to the vinyl and to one Pd atom. The barrier is 48 kcal/mol. The side-on parallel approach was suggested by Nakatsuji et al., for the activation of H_2 by Pd_d. Then the final product H−Pd−Pd−H presents a cis configuration. Blomberg et al. have found that the square configuration, where each hydrogen is attached to the two Pd atoms, is more stable by 26 kcal/mol. Therefore the side-on parallel approach is not necessarily the optimal pathway for H−H activation on Pd_d. The transition state (TS1) for C_2H_2/Pd_d side-on parallel approach gives the lowest barrier relative to di-σ adsorption, 36 kcal/mol. The main reason seems to be the participation of the second carbon atom in the interaction with the dimer, which is missing in the other transition states. The topology of the transition state is close to the di-σ adsorption. The inactive CH_2 group remains attached to one Pd atom, while the activation takes place on the other Pd atom. Here again the activation is ensured by only one Pd atom; therefore, the barrier is equal to that of the single atom.  

Our calculations show clearly that the palladium single atom and dimer activate the ethylene C−H bond. This result supports molecular beam experiments from Fayet et al. where palladium clusters with up to 25 atoms were found to activate ethylene. However, while in these experiments the dimer is more reactive than the single atom, in our calculations Pd_d and Pd present the same barrier height.
TABLE 4: Adsorption Energies (in kcal/mol) Relative to Free C₂H₄ and Pd₂ Species, the Decomposition of the Interaction Energy between C₂H₄ and Pd₂ for the Optimized C₂H₄/Pd₂ Geometry, Overall Charge Transfer (a Back-Donation to Ethylene), and Geometries (Å and deg) for π and di-σ Complexes of Pd₂(C₂H₄)

<table>
<thead>
<tr>
<th>adsorption mode</th>
<th>E_ads</th>
<th>ΔE_D</th>
<th>ΔE_elec</th>
<th>ΔE_orb</th>
<th>charge transfer</th>
<th>Pd−Pd</th>
<th>Pd−C</th>
<th>C−C</th>
<th>hydrogen dihedral angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>π</td>
<td>-23</td>
<td>+161</td>
<td>-141</td>
<td>-56</td>
<td>0.09 e⁻</td>
<td>2.86</td>
<td>2.22</td>
<td>1.40</td>
<td>99</td>
</tr>
<tr>
<td>di-σ</td>
<td>-51</td>
<td>+231</td>
<td>-195</td>
<td>-111</td>
<td>0.14 e⁻</td>
<td>2.74</td>
<td>2.12</td>
<td>1.44</td>
<td>107</td>
</tr>
</tbody>
</table>

a ΔE_D: Pauli repulsion; ΔE_elec, electrostatic interaction; ΔE_orb: orbital interaction.  

The hydrogen dihedral angle is the angle between the HCC and the CCPd planes.

TABLE 5: Ethylene Dissociation on Pdₙ

<table>
<thead>
<tr>
<th>structure</th>
<th>E_ads or barrier height</th>
<th>Pd₁−Pd₂</th>
<th>Pd₁−C/Pd₂−C</th>
<th>Pd₁−H/Pd₂−H</th>
<th>C−H</th>
<th>C−C</th>
</tr>
</thead>
<tbody>
<tr>
<td>HPd₃C₂H₃</td>
<td>-38</td>
<td>2.78</td>
<td>2.10</td>
<td>1.73</td>
<td>1.36</td>
<td></td>
</tr>
<tr>
<td>square</td>
<td>-13</td>
<td>2.66</td>
<td>1.96</td>
<td>1.56</td>
<td>1.36</td>
<td></td>
</tr>
<tr>
<td>trans</td>
<td>-9</td>
<td>2.67</td>
<td>1.96</td>
<td>1.54</td>
<td>1.34</td>
<td></td>
</tr>
<tr>
<td>cis</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>transition state</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>end-on</td>
<td>60</td>
<td>2.81</td>
<td>2.00</td>
<td>1.53</td>
<td>1.32</td>
<td></td>
</tr>
<tr>
<td>side-on perpendicular</td>
<td>48</td>
<td>2.92</td>
<td>2.12/2.13</td>
<td>1.63/2.44</td>
<td>1.60</td>
<td>1.36</td>
</tr>
<tr>
<td>side-on parallel</td>
<td>36</td>
<td>2.81</td>
<td>2.16/2.30</td>
<td>1.61/3.53</td>
<td>1.65</td>
<td>1.40</td>
</tr>
</tbody>
</table>

a The adsorption energies (in kcal/mol) for the vinyl−hydride product are relative to free C₂H₄ and Pdₙ species; the barrier heights (in kcal/mol) for the transition states are relative to the di-σ molecular complex; and the distances are in Å.

Figure 3. Various transition states for the C−H activation by Pd₂: TS1, side-on parallel approach; TS2, side-on perpendicular approach; and TS3, end-on approach.

6. Adsorption of Ethylene on Pdₙ (n = 3−6) Clusters

In this section, we present the results for the adsorption of ethylene on Pdₙ (n = 3−6) clusters. The two adsorption modes π and di-σ are studied. The most surprising result is the change in the cluster structure associated with the di-σ adsorption mode. For Pdₙ (n = 3−5) clusters, the bond between the two Pd atoms involved in the adsorption is broken (see Figure 4). Ethylene induces a reconstruction of the clusters: from the triangle toward the linear structure for Pd₃ and from the tetrahedron toward the planar structure for Pd₄. Such effects were already suggested by Parks et al. for N₂ adsorption on Niₙ clusters. In their investigation of the structure of nickel clusters, they have found that in some cases nitrogen causes a change in the cluster structure. In Figure 4 we notice that the Pd−Pd distance and therefore the distortion decreases with the cluster size. Therefore this effect will be weak on the palladium surface and will correspond to a local relaxation of the surface. The structural effect associated with the π adsorption mode is smaller, and there is an increase of the bond length between the atom involved in the adsorption and its first neighbors. This is a general trend for the adsorption on a transition metal surface, and metal atoms involved in the adsorption are often pulled out from the surface.

For the distortion of adsorbed ethylene (Table 6), we found the same trend as for the dimer, a higher distortion (rehybridization) for the di-σ adsorption mode. The C−C bond length is longer when C₂H₄ is di-σ. A comparison can be made with the benzene adsorption on Rh(111), LEED analysis has shown that the benzene is adsorbed on a 3-fold position, and then, half of the C−C bonds are on top positions and the other half are on bridge positions. In correlation with our results, the C−C bond on top (equivalent to a π adsorption) is shorter than the C−C bond on bridge (equivalent to a di-σ adsorption). The experimental value of the C−C bond for adsorbed ethylene on

![Figure 4. Cluster distortion under the di-σ adsorption mode (distances in Å).](image)

TABLE 6: Structures of π and Di-σ C₂H₄Pdₙ Complexesa

<table>
<thead>
<tr>
<th>Pdₙ</th>
<th>spin</th>
<th>Pd−Pd</th>
<th>C−C</th>
<th>hydrogen dihedral angle</th>
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<td>S</td>
<td>2.86</td>
<td>1.40</td>
<td>98</td>
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<tr>
<td>2</td>
<td>T</td>
<td>2.77</td>
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<td>3</td>
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<td>2.81</td>
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<td>6</td>
<td>T</td>
<td>2.84</td>
<td>1.39</td>
<td>105</td>
</tr>
</tbody>
</table>

a Spin (S for singlet and T for triplet), Pd−Pd distance (Å) of atoms involved in the adsorption and the geometry of adsorbed ethylene (Å and deg).
Pd(111),\textsuperscript{30} 1.43 Å, is close to the calculated values for the di-σ adsorption mode, 1.42–1.46 Å. However, HREELS experiments support a π adsorption on Pd(111)\textsuperscript{3} and Pd(110),\textsuperscript{5} whereas for Pd(100)\textsuperscript{1} both π and di-σ modes were observed. Table 6 also shows the spin state of the C\textsubscript{2}H\textsubscript{4}Pd\textsubscript{n} complexes. In the di-σ adsorption, the reaction between ethylene and the cluster can be described as an oxidative addition reaction in which the π bond of ethylene is broken and two metal–carbon σ bonds are formed. Therefore all the di-σ complexes are singlet except the C\textsubscript{2}H\textsubscript{4}Pd\textsubscript{3} complex where the distortion of ethylene is the smallest. The distortion of ethylene is smaller in the π adsorption and the spin of the cluster is not perturbed. Therefore all the π complexes except the C\textsubscript{2}H\textsubscript{4}Pd\textsubscript{3} complex are triplet. The latter is singlet because the single atom Pd(d\textsuperscript{10}) is singlet.

The evolution of the adsorption energy with the cluster size is sketched in Figure 5. The adsorption energy oscillates and decreases with the cluster size toward the experimental value, 13 kcal/mol.\textsuperscript{21} Chemical physics of gas-phase clusters\textsuperscript{28,32} show that reactive properties of small metal clusters are different from those of the bulk. In some cases the change in the cluster size by one metal atom can be accompanied by a large change in the reactivity, and curves like Figure 5 were often found in experiments. We notice that for Pd\textsubscript{n} (n = 3–5) clusters, which collapse under the di-σ adsorption, the best adsorption mode is π, whereas the Pd\textsubscript{2} and Pd\textsubscript{6}, which give π and di-σ distortions of the same magnitude, the di-σ adsorption is more favorable.

### 7. Conclusion

In this work we have presented density functional calculations on the adsorption of ethylene on small palladium clusters, Pd\textsubscript{n} (n = 1–6). The adsorption mode can be π or di-σ according to the cluster size. The adsorption energy oscillates and decreases with the cluster size toward the experimental value. The π adsorption is maximum for the single atom, whereas the di-σ adsorption is maximum for the dimer. Pd\textsubscript{2} (n = 3–5) clusters are not stable against adsorption, they undergo structural changes to accommodate ethylene. The Pd–Pd bond for atoms involved in the di-σ adsorption is broken. Ethylene shows a stronger rehybridization with the di-σ adsorption, the C–C bond length and the hydrogen dihedral angle are large compared with the values obtained with the π adsorption. Both the single atom and the dimer activate the C–H bond of ethylene in agreement with the molecular beam experiments in the gas phase. The potential energy surfaces are characterized by very stable molecular complexes compared with vinyl–hydrate products. These potentials show that the d\textsuperscript{10} configuration (the single atom) is appropriate for the π interaction, whereas the d\textsuperscript{5}s\textsuperscript{1} configuration is appropriate for the di-σ interaction (the dimer is d\textsuperscript{9}s\textsuperscript{1}s\textsuperscript{1}).

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### References and Notes

19. (b) Handbook of Chemistry and Physics; West, R. C., Ed.; CRC: Cleveland, 1986.