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The adsorption of ethylene on the (110) surfaces of copper, silver and platinum: a DFT study

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Abstract

Density functional theory calculations have been performed for the adsorption of the ethylene molecule on the (110) surfaces of platinum, silver and copper. The cluster model approach has been used to model the metal surfaces. For each metal surface, four adsorption sites have been considered: the atop site, the shortbridge site, the longbridge site and the trough site. For each case, optimized geometries and adsorption energies have been calculated. Vibrational wavenumber calculations have been performed for the energetically more favored adsorption modes on each metal surface. The results show that on the (110) surfaces of copper and silver, the ethylene molecule adsorbs preferentially above the close-packed rows of metal atoms of the first layer, the atop adsorption site being slightly preferred over the shortbridge site on both metal surfaces. On the (110) surface of platinum a comparison between our results and the available experimental results suggests that beyond the thermodynamic factors, kinetic factors may play an important role on the adsorption process. The results also show that upon adsorption, both the degree of distortion of the ethylene molecule (relative to its gas phase geometry) and the binding strength to the metal surface increase in the order $Ag < Cu \ll Pt$. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Chemisorption; Clusters; Density functional calculations; Single crystal surfaces; Vibrations of adsorbed molecules

1. Introduction

The exact knowledge of the adsorption mode of the ethylene molecule on transition-metal surfaces is of importance for the understanding of catalytic reactions involving this small olefin. For this reason, in the last two decades, numerous experimental studies of the adsorption of ethylene on a variety of transition-metal surfaces have been performed. These studies have led to the general conclusion that, at low temperatures ($\cong 100$ K), the ethylene molecule adsorbs molecularly on the transition-metal single crystal surfaces and for low adsorbate coverages, the CC bond in adsorbed ethylene lies parallel to the surface. Although the type of bonding differs depending on the electronic and geometric structure of the surface, in all cases, the main interaction with the metal surface is through the electrons in the CC bond thus causing an elongation of the carbon–carbon bond, which is accompanied by a bending of the hydrogens away from the surface. Experimentally, the measurement of the vibrational frequency of the ν_2(CC) stretching mode, has been perhaps the most straightforward method for determining the state of hybridization of the adsorbed molecule, due to the high sensitivity of the CC stretching frequency to the hybridized state of the two carbon atoms. For example, ν(CC) is 1623 cm^{-1} for gaseous C_2H_4 and

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is 993 cm^{-1} for gaseous C_2H_6, which represent sp^2 and sp^3 hybridized systems, respectively.

Whereas the adsorption of ethylene on the clean (111) surfaces of copper [1–5] and platinum [6–16] has already been extensively studied both by experimental [1,2,6–10] and by theoretical [2–5,11–16] techniques, the adsorption on the corresponding (110) surfaces has received considerably less attention [17–23]. In what concerns the adsorption of ethylene on single crystal silver surfaces, several studies may be found in the literature [24–32], some of them refering to the adsorption on a (110) surface [24–27].

On an earlier study of the adsorption of C_2H_4 on a Cu(110) surface, Ritz et al. [17] using ultraviolet photoelectron spectroscopy (UPS), concluded that the ethylene molecule adsorbs on the atop sites (π adsorption mode). Most recently, Raval et al. [18] also concluded that the pattern of frequencies follows that reported for a π complex. Schaff et al. [19] using photoelectron diffraction concluded that the molecule adsorbs on the close-packed rows with the CC axis parallel to the surface and oriented in the $\langle 110 \rangle$ direction. Their data indicated that ethylene adsorbs on Cu(110) in either an atop site at a perpendicular height of 2.08 ± 0.02 Å with a CC bond length of 1.32 ± 0.09 Å, or in a shortbridge site at a perpendicular height of 2.09 ± 0.02 Å with a CC bond length of 1.53 ± 0.13 Å. Doering et al. [20] using STM, concluded also that the molecule adsorbs on the close-packed rows of copper atoms of the first layer, oriented in the $\langle 110 \rangle$ direction and suggested that the shortbridge site is the most probable adsorption site but the adsorption on the atop site could not be ruled out.

On an earlier study of the adsorption of C_2H_4 on a Ag(110) clean surface, Backx et al. [24] using electron energy loss spectroscopy studies (EELS) concluded that C_2H_4 adsorbs with its CC bond parallel to the surface and the geometry of the molecule remains nearly unchanged. According to them the activation energy of desorption is $\cong 40$ kJ mol^{-1}. Krüger et al. [25] using several experimental techniques, concluded that at low temperatures (110 K) ethylene adsorbs molecularly on Ag(110) in the π adsorption mode, with its CC bond parallel to the surface and the geometry of the molecule remains almost undisturbed upon adsorption. The same conclusions have also been reached by Wang et al. [26] using solid-state ^{13}C NMR and by Solomon et al. [27] using NEXAFS. Studies of the adsorption of C_2H_4 on other silver surfaces [30–32] have also led to the conclusion that the metal–adsorbate interaction is weak and the molecular geometry is little perturbed upon adsorption. The theoretical studies found in the literature, of the adsorption of C_2H_4 on silver surfaces, are very scarce. A theoretical study [28] of the interaction of Ag_2 with various adsorbates including ethylene has been performed, revealing an adsorption energy of less than 40 kJ mol^{-1}. Some electronic structure calculations of the interaction of ethylene with a Ag_3 cluster have also been conducted by Carter et al. [29]. However, to our knowledge, the adsorption of ethylene on larger silver clusters has not yet been investigated theoretically.

The Pt(110) surface, shows two metastable reconstructions called $(1*1)$ and $(2*1)$ Pt(110), the $(1*1)$ reconstruction being less stable than the $(2*1)$ reconstruction. Hence, the adsorption of ethylene on the $(1*1)$-Pt(110) surface has received little attention [21–23]. However, the $(1*1)$ reconstruction of Pt(110) can be formed via a procedure developed by Bonzel et al.[33], and some recent experimental studies [21,22,34] showed that the $(1*1)$ reconstruction of Pt(110) shows a very peculiar reactivity, being unusually active for carbon–carbon bond scission and coke formation. According to EELS [21], at 93 K, ethylene adsorbs as a π-bound complex. Upon heating to 160 K the π-bound ethylene is partially converted to a di-σ species. In the only known theoretical study on the adsorption of C_2H_4 on a $(1*1)$-Pt(110) surface, Maurice et al. [23], using the extended Hückel theory concluded that the di-σ coordination of the CC double bond on the shortbridge and longbridge sites between the metal atoms of the topmost layer was favored.

A large variety of experimental techniques are available nowadays to gain some knowledge on the adsorption sites and the orientation of adsorbed molecules. Yet, in general, experimental data alone are not sufficient to obtain a consistent and complete picture of the structure of adsorption complexes. Supporting theoretical investigations are therefore necessary.

The aim of the present study is to compile theoretical results for the adsorption of ethylene on the (110) surfaces of copper, silver and platinum, under the same conditions in terms of methodology, cluster structure and basis sets, in order to determine the

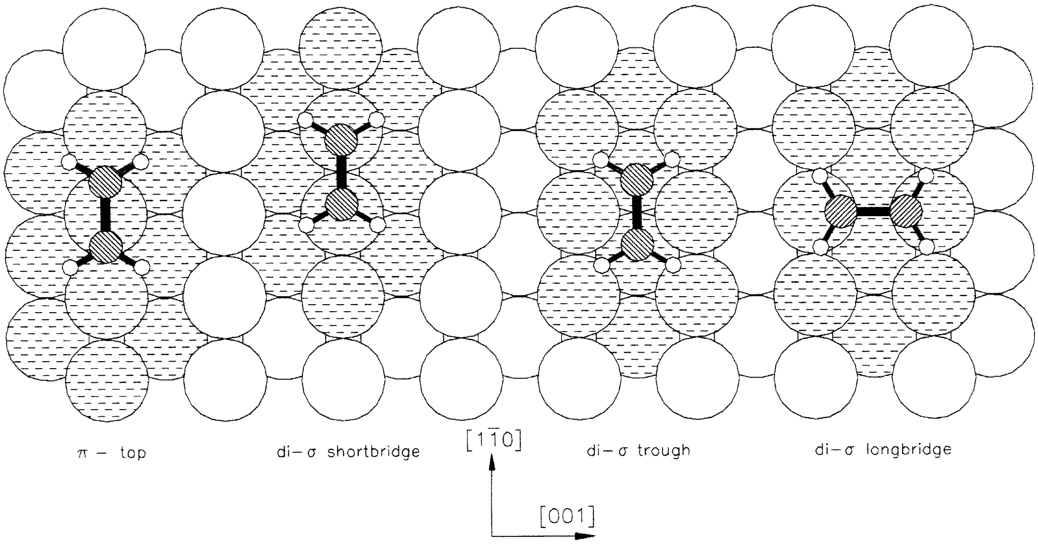

Fig. 1. Schematic view of the several 'adsorbate/metal cluster' systems used in the present study: atop-$C_2H_4/M_{10}(4,6)$, shortbridge-$C_2H_4/M_{10}(4,6)$, trough-$C_2H_4/M_{10}(6,4)$ and longbridge-$C_2H_4/M_{10}(6,4)$, with M = Pt, Ag and Cu. Only the shaded metal atoms were included in the C_2H_4/M_{10} calculations. The unshaded metal atoms were included in the picture only to better illustrate several possible adsorption modes of ethylene on a (110) surface of a metal with a face-centered cubic crystal structure.

preferred adsorption modes on each metal surface and to understand the trend in the adsorption of this species on these three metal surfaces. The cluster model approach will be used along this work.

During the last years, several different theoretical models have been used, to study catalytic reactions at solid surfaces. These models may be finite (clusters, finite cube) or infinite (periodic systems). The advantages and disadvantages of all of these models have already been thoroughly discussed in the literature [35]. Metal clusters have since long been one of the most common approaches used, to model metal surfaces. This approach is a straightforward consequence of the idea that adsorption is a local phenomenon. Quantum chemical research on clusters has become very fruitful especially due to advances in the development of density functional theory techniques and the incorporation of gradient correction terms to the exchange-correlation energy.

This paper is organized as follows. In Section 2 we describe the details of the computational method used and of the metal clusters used to describe the metal surface. In Section 3, we report and discuss the results obtained for the adsorption of the ethylene molecule on the atop, shortbridge, longbridge and trough sites of the (110) surfaces of copper, silver and platinum. Some general conclusions are summarized in Section 4.

2. Method

In the present work, the interaction of the ethylene molecule with the (110) surfaces of platinum, silver and copper was studied using the cluster model approach. All these metals have a face-centered cubic (f.c.c.) crystal structure. The metal surfaces were modeled by a two-layer cluster of C_{2V} symmetry, with 6 metal atoms in one layer and 4 metal atoms in the other layer. To study the adsorption on the atop and shortbridge sites we used a $M_{10}(4,6)$ cluster as shown in Fig. 1, where the numbers inside brackets indicate the number of metal atoms in the first and second layer, respectively. To study the adsorption on the longbridge and trough sites we used the same cluster but on an inverted position, that is, we used a $M_{10}(6,4)$ cluster as shown in Fig. 1. It must be stressed that in all these clusters, *all the metal atoms* were described by the large LANL2DZ basis set. This basis set treats the outer 18 electrons of the platinum

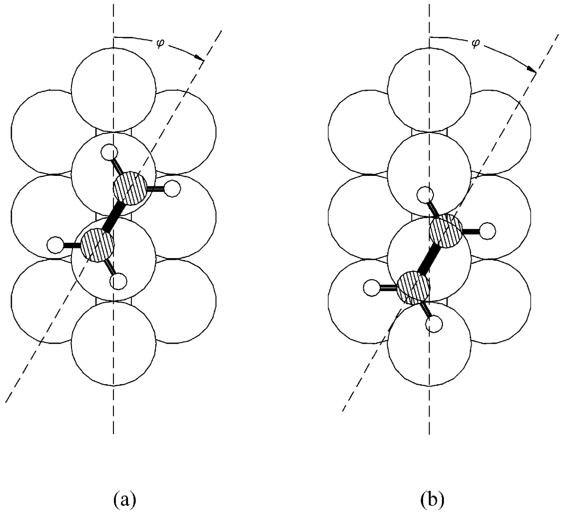

Fig. 2. Rotation of the C_2H_4 molecule on a Pt_{10} cluster: (a) From shortbridge ($\varphi = 0°$) to cross-shortbridge ($\varphi = 90°$) and (b) From atop ($\varphi = 0°$) to cross-atop ($\varphi = 90°$).

atoms and the outer 19 electrons of copper and silver atoms with a double zeta basis set and treats all the remainder electrons with the effective core potential of Hay and Wadt [36].

The non-metallic atoms (C and H) were described by the 6-31G** basis set of double zeta quality with p polarization functions in hydrogen atoms and d polarization functions in carbon atoms. In all the clusters the nearest-neighbor distances were taken from the bulk and are 2.77483 Å for platinum, 2.88874 Å for silver and 2.55612 Å for copper. These clusters form compact sections of the corresponding ideal surfaces. There are many examples in the literature where small cluster models, often smaller than those used in the present study have proved very useful in the study of the adsorption of individual species on metal surfaces and have provided accurate descriptions of adsorbate structures, vibrations and chemisorption energies. The use of larger clusters in the present work would be inaccessible given the number of valence electrons explicitly considered, the basis set quality and the computing power available in this study.

Density functional theory (DFT) calculations were used to obtain the geometries, adsorption energies and frequencies for the ethylene molecule adsorbed in the four different adsorption modes on the (110) surfaces of all the transition metals cited earlier. The B3LYP hybrid method proposed by Becke [37] and included in the GAUSSIAN 98 [38] package was used. This method includes a mixture of Hartree–Fock and DFT exchange terms associated with the gradient corrected correlation functional of Lee et al.[39].

In order to reduce the size of the calculations, in the study of all the adsorption modes the CC bond of ethylene was forced to be parallel to the surface. This approach is fully supported by the available experimental information. In all the calculations the ethylene molecule was forced to have a plane of symmetry that contains the CC bond and is perpendicular to the surface. In the study of the adsorption on the shortbridge, longbridge and trough sites the symmetry of the overall system M_{10}/C_2H_4 was C_{2V}. In the study of the adsorption on the atop site, we forced the center of the CC bond to be directly above one metal atom of the first layer being C_S the overall symmetry of the system.

For reasons that are mentioned in Section 3.4, in the study of the C_2H_4–Pt(110) adsorption system, the rotation of the ethylene molecule above the longbridge, shortbridge and atop adsorption sites has also been studied. In this study, for each adsorption site, the ethylene molecule was forced to rotate by 90° (three increments of 30° each, starting from the corresponding orientations shown in Fig. 1) around an axis that passes through the middle of the CC bond and is perpendicular to the surface. This is showed in Fig. 2 for the rotations from shortbridge to cross-shortbridge and from atop to cross-atop. For each increment of 30°, the perpendicular distance from the CC bond to the surface, as well as the internal geometric parameters of the C_2H_4 molecule, were fully optimized. In these calculations the CC bond was also forced to be parallel to the surface and the molecule was also forced to have a plane of symmetry that contains the CC bond and is perpendicular to the surface.

The determination of the adsorption energies has been one of the most critical and controversial aspects of the cluster modeling of surfaces and several different ways, such as, for example, the bond preparation approach [40], have already been proposed in order to improve their calculation. However, these alternative ways are not always straightforward and are often ambiguous. So in our calculation of the adsorption energies, the energies of the lowest spin multiplicity clusters and the energy of the lowest spin multiplicity

Table 1
Optimized geometry and C–C MOP for the free C_2H_4 molecule

C_2H_4	Theoretical values	Experimental values[a]
Distance (CC) (Å)	1.3306	1.337 ± 0.003
Distance (CH) (Å)	1.0868	1.086 ± 0.003
Angle (HCC) (°)	121.818	121.35 ± 1
Angle ((CH$_2$)–C) (°)	180.000	180.00
C–C (MOP) (a.u.)	1.3682	–

[a] Ref. [41].

gas phase ethylene molecule have been used as reference.

3. Results

3.1. Free C_2H_4 molecule

The free ethylene molecule was optimized at the B3LYP/6-31G** level. The computed geometry and C–C Mulliken overlap population (MOP) are listed in Table 1 along with the corresponding experimental values [41]. Note that, we will always refer to the angle (CH$_2$)–C as being the angle between the HCH plane and the CC bond. This is exemplified in Fig. 3. Vibrational frequency calculations were also performed, and the results are shown in Table 2 along with the corresponding experimental values [42]. The agreement between the theoretical results in Tables 1 and 2 and the corresponding experimental results is good.

3.2. C_2H_4/Cu(110)

The optimized geometries, adsorption energies, MOPs of some relevant bonds and total adsorbate charges obtained for the adsorption of the ethylene molecule on the several adsorption sites on a Cu(110) surface are listed in Table 3. Note that, the C_2H_4-surface distance is defined as being the perpendicular distance between the CC bond and a plane containing the nucleus of the metal atoms of the first layer.

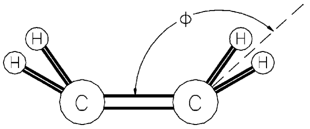

Fig. 3. The angle (CH$_2$)–C.

Table 2
Vibrational frequencies (cm^{-1}) of the free C_2H_4 molecule. Values inside brackets are scaled by a factor of 0.9614 (Ref. [43])

Mode	Theoretical values	Experimental values[a]
ν_{10}, $\rho(CH_2)$	831 (799)	826 (IR)
ν_8, $\omega(CH_2)$	961 (924)	940 (R)
ν_7, $\omega(CH_2)$	976 (938)	949 (IR)
ν_4, $\tau(CH_2)$	1069 (1028)	Forbidden
ν_6, $\rho(CH_2)$	1240 (1192)	1222 (R)
ν_3, $\delta(CH_2)$	1387 (1333)	1342 (R)
ν_{12}, $\delta(CH_2)$	1482 (1425)	1444 (IR)
ν_2, $\nu(CC)$	1714 (1648)	1623 (R)
ν_{11}, $\nu_s(CH_2)$	3147 (3025)	2989 (IR)
ν_1, $\nu_s(CH_2)$	3162 (3040)	3026 (R)
ν_5, $\nu_a(CH_2)$	3223 (3098)	3103 (R)
ν_9, $\nu_a(CH_2)$	3248 (3122)	3105 (IR)

[a] Ref. [42].

Our results show that the adsorption strength of C_2H_4 on a Cu(110) surface is not very strong and the adsorption sites on the close-packed rows of Cu atoms with the CC axis oriented in the ⟨110⟩ crystal azimuth are clearly favored over the other two possible adsorption sites considered. This is in good agreement with experimental observations.

Upon adsorption on the two most favored adsorption sites, the C–C bond length increased from 1.3306 Å (gas phase) to 1.3638 Å (atop) and 1.3528 Å (shortbridge) and the (CH$_2$)–C angle decreased from 180° (gas phase) to 171.25° (atop) and 174.05° (shortbridge). The elongation of the C–C bond was accompanied by a dropping of the C–C MOP from 1.3682 (gas phase) to 1.0409 (atop) and 1.0876 (shortbridge). According to our results the atop adsorption site is energetically more favored than the shortbridge adsorption site (-58.1 vs -47.5 kJ mol^{-1}). This is in agreement with the calculated geometrical parameters for the adsorption on both sites, which show that when adsorbed on the atop site, the ethylene molecule is slightly more distorted (relatively to its gas phase geometry) than when adsorbed on the shortbridge site.

Schaff et al. [19] determined experimentally that ethylene adsorbs on a Cu(110) surface in either an atop site or in a shortbridge site, being the geometrical parameters for adsorption on both sites very different

Table 3
Adsorption energies (kJ mol^{-1}), optimized geometries, MOPs of some relevant bonds and total adsorbate Mulliken charges, Q, for C_2H_4 adsorbed on the shortbridge, longbridge, atop and trough sites, on a Cu(110) surface. The C–Cu MOP is the MOP between each carbon atom and its nearest copper atom

C_2H_4/Cu(110)	Atop	Shortbridge	Longbridge	Trough
Adsorption energy (kJ mol^{-1})	− 58.1	− 47.5	− 10.8	− 7.3
Distance C_2H_4-surface (Å)	2.2596	2.3800	3.1161	3.3642
Distance CC (Å)	1.3638	1.3528	1.3366	1.3338
Distance CH (Å)	1.0857	1.0875	1.0866	1.0867
Angle CCH (°)	120.823	121.111	121.649	121.775
Angle ((CH_2)–C) (°)	171.254	174.057	178.705	179.595
C–C MOP (a.u.)	1.0409	1.0876	1.2762	1.3000
C–Cu MOP (a.u.)	0.2881/0.1151[a]	0.2540	0.0628	0.0282
$Q_{\text{adsorbate}}$ (Mulliken) (a.u.)	+ 0.2613	+ 0.2823	+ 0.0938	+ 0.0786

[a] In this case, due to the lower C_s symmetry of the C_2H_4/Cu_{10} system, the two carbon atoms have different electronic populations.

from each other. There is a much better agreement between our calculated geometrical parameters for adsorption on the atop site and the corresponding values referred by Schaff et al., than between our calculated values for adsorption on the shortbridge site and the corresponding values referred by Schaff et al. For the adsorption on the atop site, the computed value of the CC distance (1.3638 Å) lies in the experimental error bar (1.32 ± 0.09 Å), the computed value of the perpendicular height above the surface (2.2596 Å) being larger than that referred by Schaff et al. (2.08 ± 0.02 Å). For the adsorption on the shortbridge site, both the computed value of the CC distance (1.3528 Å) and of the perpendicular height above the surface (2.3800 Å) are very different from the corresponding values referred by Schaff et al. (1.53 ± 0.13 Å and 2.09 ± 0.02 Å, respectively). This observation also supports the idea that the atop site adsorption hypothesis of Schaff et al. [19] should be the correct one.

Table 4
Calculated vibrational frequencies (cm^{-1}) for C_2H_4 adsorption on the shortbridge and atop adsorption modes, on a Cu(110) surface. The theoretical values are not scaled by any factor

C_2H_4/Cu (110)	Experimental[a]	Shortbridge	Atop
ν_s (C–Cu)	–	139	157
ν_{10}, $\rho(CH_2)$	–	841	843
ν_7, $\omega(CH_2)$	–	966	918
ν_3, $\delta(CH_2)$	1275	1348	1327
ν_2, ν(CC)	1534	1636	1605
ν_1, $\nu_s(CH_2)$	–	3152	3166

[a] Ref. [18].

Vibrational frequencies have been calculated, at the minima geometries for the two most favored adsorption modes, and the results are shown in Table 4. Note that for reasons of simplicity, we will always refer to the vibrational modes of the adsorbed ethylene molecule by the mode numbers derived for the free molecule. The ν(C–Cu) stretching frequency is higher for adsorption on the atop site than on the shortbridge site, indicating a stronger metal–adsorbate bond in the former case. For both adsorption modes, the available experimental frequencies are lower than the corresponding calculated results. However, there is a better agreement between the experimental results and the calculated results for adsorption on the atop site.

3.3. C_2H_4/Ag(110)

Table 5 summarizes the computed geometries, adsorption energies, MOPs of some relevant bonds and total adsorbate charges obtained for the adsorption of the ethylene molecule on several adsorption sites on a Ag(110) surface. The results show that the ethylene molecule adsorbs weakly on the Ag(110) surface and its geometric and electronic structure are little perturbed by the adsorption process.

The results obtained show that the ethylene molecule adsorbs above the close-packed rows of Ag atoms of the first layer. Although the difference in adsorption energy between the atop and the shortbridge sites is small, our results show that the

Table 5
Adsorption energies (kJ mol^{-1}), optimized geometries, MOPs of some relevant bonds and total adsorbate Mulliken charges, Q, for C_2H_4 adsorbed on the shortbridge, longbridge, atop and trough sites, on a Ag(110) surface. The C–Ag MOP is the MOP between each carbon atom and its nearest silver atom

C_2H_4/Ag(110)	Atop	Shortbridge	Longbridge	Trough
Adsorption energy (kJ mol^{-1})	− 33.8	− 26.8	− 7.1	− 5.5
Distance C_2H_4–surface (Å)	2.6668	2.7912	3.3987	3.8959
Distance CC (Å)	1.3480	1.3432	1.3344	1.3326
Distance CH (Å)	1.0861	1.0872	1.0868	1.0868
Angle CCH (°)	121.363	121.415	121.713	121.786
Angle ((CH_2)–C) (°)	176.459	176.611	179.087	179.528
C–C MOP (a.u.)	1.1501	1.1899	1.3083	1.3266
C–Ag MOP (a.u.)	0.1962/0.1025[a]	0.1380	0.0459	0.0203
$Q_{\mathrm{adsorbate}}$ (Mulliken) (a.u.)	+ 0.2270	+ 0.2077	+ 0.0706	+ 0.0525

[a] In this case, due to the lower C_s symmetry of the C_2H_4/Ag_{10} system, the two carbon atoms have different electronic populations.

adsorption on the atop site is the preferred one. This is in agreement with the experimental observations of Krüger et al. [25], Wang et al. [26] and Solomon et al. [27] who have also concluded that the π adsorption mode was the most favored one. Our result obtained for the adsorption energy on the atop site (33.8 kJ mol^{-1}) is also in fairly good agreement with the reported value of 40 kJ mol^{-1} [24,28] for the energy of desorption of C_2H_4 from an Ag(110) surface.

Table 6 shows the results obtained in the vibrational frequency calculations for the adsorption on the two most favored adsorption sites. No experimental values were found in the literature for the adsorption of C_2H_4 on a clean Ag(110) surface. The low ν_s(C–Ag) frequencies obtained for both adsorption modes, shows that the binding strength of C_2H_4 on a Ag(110) surface is small. A comparison between the values in Table 6 and the values in Table 2 shows that the vibrational wavenumbers of the adsorbed ethylene molecule on an Ag(110) surface are not very different from the corresponding values on the free C_2H_4 molecule. This also supports the conclusion that the binding energy of C_2H_4 on a Ag(110) surface is small.

Table 6
Calculated vibrational frequencies (cm^{-1}) for C_2H_4 adsorption on the shortbridge and atop adsorption modes, on a Ag(110) surface. These theoretical values are not scaled by any factor. No experimental values were found in the literature for the adsorption of C_2H_4 on a clean Ag(110) surface

C_2H_4/Ag(110)	Shortbridge	Atop
ν_s (C–Ag)	102	114
ν_4, $\tau(CH_2)$	1060	1042
ν_7, $\omega(CH_2)$	988	971
ν_2, ν(CC)	1666	1651
ν_3, $\delta(CH_2)$	1368	1362
ν_1, $\nu_s(CH_2)$	3157	3167

3.4. C_2H_4/Pt(110)

The optimized geometries, adsorption energies, adsorbate charges and the MOPs of the most relevant bonds, obtained for the adsorption of C_2H_4 on four different sites on a Pt(110) surface are presented in Table 7. Unlike what happened in the previous metals, the results presented in Table 7 show that the ethylene molecule binds very strongly on the longbridge, shortbridge and atop sites of the Pt(110) surface, and there is a clear rehybridization of the carbon atoms toward the sp^3 configuration. The perpendicular C–Pt distances are much shorter than the corresponding distances on the other metal surfaces considered earlier, which is in agreement with the higher adsorption energies observed. According to our results, the adsorption energy and the distortion of the ethylene molecule is higher in the longbridge site. For the longbridge adsorption site the increase of the CC bond length is 0.1924 Å giving a distance of 1.5230 Å, which is very close to the single-bond CC distance in ethane (1.536 Å).

Vibrational frequencies have been calculated, at the minima geometries for the three most favorable adsorption modes and the results are shown in Table

Table 7
Adsorption energies (kJ mol^{-1}), optimized geometries, MOPs of some relevant bonds and total adsorbate Mulliken charges, Q, for C_2H_4 adsorbed on the shortbridge, longbridge, atop and trough sites of the Pt(110) surface. The C–Pt MOP is the MOP between each carbon atom and its nearest platinum atom

C_2H_4/Pt(110)	Longbridge	Shortbridge	Atop	Trough
Adsorption energy (kJ mol^{-1})	− 200.9	− 173.3	− 148.5	− 20.5
Distance C_2H_4-surface (Å)	1.6734	1.9755	2.0674	3.1248
Distance CC (Å)	1.5230	1.4864	1.4214	1.3354
Distance CH (Å)	1.0965	1.0931	1.0854	1.0865
Angle CCH (°)	109.893	114.729	119.374	121.841
Angle ((CH_2)–C) (°)	126.698	139.052	158.355	180.305
C–C MOP (a.u.)	0.7010	0.6397	0.7291	1.2905
C–Pt MOP (a.u.)	0.5536	0.5602	0.3690/0.3047[a]	0.0126
$Q_{\mathrm{adsorbate}}$ (Mulliken) (a.u.)	+ 0.1596	+ 0.1430	+ 0.3590	+ 0.1076

[a] In this case, due to the lower symmetry of the C_2H_4/Pt_{10} system, the two carbon atoms have different electronic populations.

8. An observation of the results presented in Table 8, reveals that in this case, it is not very straightforward to draw conclusions by simply comparing the calculated results with the available experimental results. Unlike what might have been expected (considering the energetic and geometric results of Table 7), the results that are in better agreement with the available experimental results, are not the results for the adsorption on the longbridge site. In what concerns to the vibrational mode that experimentally has the most significant importance on the determination of the adsorption site of C_2H_4 on metal surfaces, namely the stretching mode ν_2(CC), the calculated result for the adsorption on the atop mode (1202 cm^{-1}) is by far, the one that is closest to the available experimental result (1210 cm^{-1}). The agreement between the calculated frequencies ν_3 and ν_7 and the corresponding experimental results is also better for the adsorption on the atop site than on the other adsorption sites.

Table 8
Experimental and calculated vibrational frequencies (cm^{-1}) for C_2H_4 adsorption on the shortbridge, longbridge and atop sites, on a Pt(110) surface. The theoretical values are not scaled by any factor

C_2H_4/Pt(110)	Experimental[a]	Shortbridge	Longbridge	Atop
ν_s (C–Pt)	410	467	421	344
ν_4, $\tau(CH_2)$	810	788	768	886
ν_7, $\omega(CH_2)$	950	1080	1130	988
ν_2, ν(CC)	1210	1044	995	1202
ν_3, $\delta(CH_2)$	1560	1477	1442	1528
ν_1, $\nu_s(CH_2)$	2960	3074	3023	3159

[a] Ref. [21].

As was mentioned on Section 1, on the only known experimental determination of the adsorption mode of C_2H_4 on a Pt(110) surface, Yagasaki et al. [21] concluded that at 93 K, C_2H_4 adsorbs as a π complex. As was also mentioned on Section 1, in the only known theoretical study of the adsorption of C_2H_4 on a (1 * 1)-Pt(110) surface, Maurice et al.[23], based only on energetic considerations, concluded that the longbridge and shortbridge sites were the most favored sites for the adsorption of C_2H_4 on a (1 * 1)-Pt(110) surface.

These apparent contradictions suggest us that some effect, other than the adsorption energy, may play an important role in the determination of the preferred adsorption mode of C_2H_4 on a (1 * 1)-Pt(110) surface. Namely, important steric effects during the adsorption process may also be involved. In order to understand this in more detail, we have studied the effect of rotating the C_2H_4 molecule, above each of the three most stable adsorption sites, while keeping its CC bond parallel to the surface (see Section 2 for more details). The corresponding energy profile is shown in Fig. 4. The rotation of the ethylene molecule from the longbridge (0°) to the trough (90°) adsorption mode, causes a great and steady decrease of the adsorption energy. The rotation from the shortbridge (0°) to the cross-shortbridge (90°) adsorption mode also causes a significant destabilization of the system. However, in this case the decrease in the adsorption energy is more irregular and it happens mainly between the 30 and

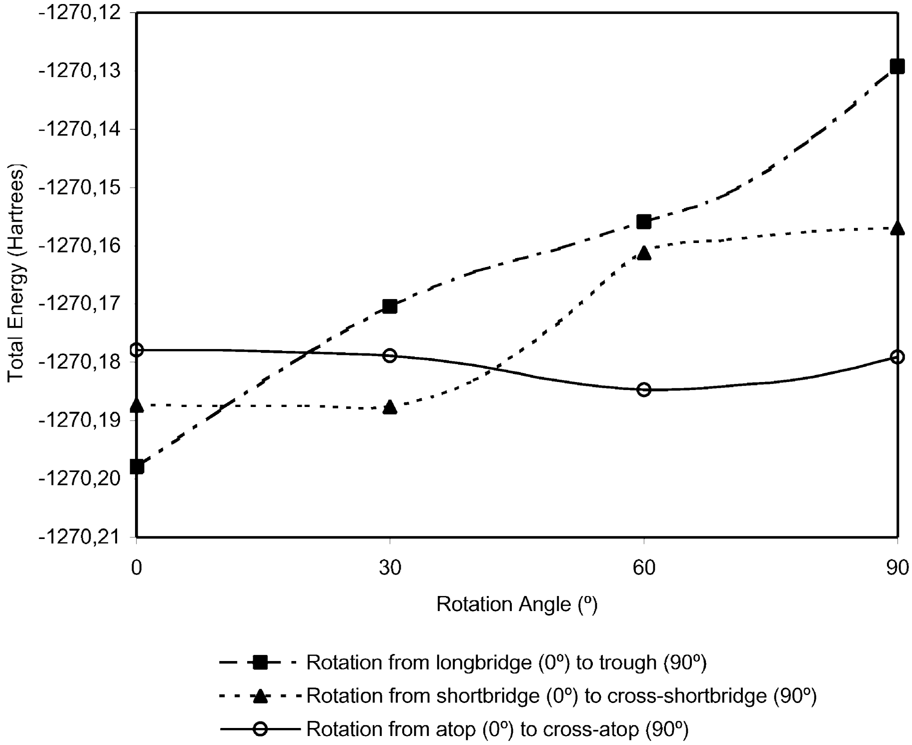

Fig. 4. Energy profile corresponding to the rotation by 90° of the ethylene molecule above the three most favored adsorption sites on a (1 * 1)-Pt(110) surface.

60°. In contrast, when adsorbed on the atop site, the C_2H_4 molecule can rotate much more freely. In this case, a rotation of the molecule by 30, 60 or 90° causes only a very small change in the adsorption energy.

All these observations seem to indicate that when a C_2H_4 molecule approaches (vertically) a longbridge site on the (1 * 1)-Pt(110) surface, direct adsorption can only occur if the molecule has a very specific orientation appropriate for the formation of the two C–Pt bonds. In this very specific orientation, the four atoms directly involved in the formation of new bonds (two C–Pt bonds) are in the same plane. In contrast, when a C_2H_4 molecule approaches (vertically) an atop site, all the possible approaching orientations (with the CC bond parallel to the surface) are likely to be very favorable. In what concerns to this stereo-specificity required for direct adsorption, the adsorption on the shortbridge site represents an intermediate case. For all these reasons, the probability of direct adsorption into the atop site must be much greater than the probability of direct adsorption on the other sites. Thus, it is our belief that, at very low temperatures, the adsorption of C_2H_4 on a (1 * 1)-Pt(110) surface, occurs mainly on the atop sites, because the direct adsorption on this site has a much greater probability of occurrence. Furthermore, it is also our belief that, at very low temperatures, the transformations from atop adsorption to the other more stable adsorption modes (longbridge and shortbridge) does not occur because these transformations are, most likely, activated processes. Elastic band calculations of C_2H_4 on a Pt(111) surface [44] have shown that the transformation from atop-adsorbed ethylene to bridge-adsorbed ethylene is an activated process. These reasons explain why, at very low temperatures, only the atop adsorption mode is observed.

Despite all these considerations about the apparent contradiction between the energy calculations and the vibrational frequency calculations, we have to admit that this contradiction may also result from the problems inherent to the cluster modeling of metal surfaces. It is not unquestionable that the relatively small Pt_{10} cluster (without embedding) used in the present work can give a good description of the corresponding metallic surface and an unbiased description of the different adsorption modes. In particular due to the problem of the dangling bonds, the atoms at the periphery of the cluster are more poorly described than the atoms in the center of the cluster. Thus, new experimental vibrational studies and also a more detailed theoretical study using larger clusters and more powerful computational means, seem highly desirable in order to gain more insight into the details of the adsorption geometry of ethylene on $(1 * 1)$-Pt(110).

4. Conclusions

In this work, we have studied the adsorption of ethylene on the (110) surfaces of platinum, silver and copper using clusters with 10 atoms to model the surfaces. Despite the limited size of the clusters, some very interesting features of the systems 'adsorbate–metal surfaces' were determined, namely adsorbate geometries, adsorption energies and vibrational frequencies. According to our results, the adsorption energy of the ethylene molecule on a metallic surface depends strongly on the electronic structure of that surface and on the adsorption site.

The results show that the ethylene molecule adsorbs strongly on the Pt(110) surface and the geometric and electronic structure of the molecule are strongly perturbed upon adsorption: there is a lengthening of the CC bond and a rehybridization of the carbon atoms from sp^2 toward sp^3. Our calculations also suggest that, although the longbridge and shortbridge adsorption modes are the most stable, they are not found at very low temperatures because the direct adsorption of C_2H_4 on these sites is likely to be hindered by the narrow adsorption channel created by the very specific orientation of the molecule required for strong interaction. Instead, the adsorption occurs mainly in the atop site, because the adsorption on this site is very favorable for any approaching orientation of C_2H_4 (with the CC bond parallel to the surface).

According to our results, on the (110) surfaces of silver and copper the binding is much weaker and on both surfaces the atop adsorption mode is energetically slightly preferred over the shortbridge adsorption mode.

Despite the interesting results presented in this paper, it must be noted that it is not unquestionable that a piece of metal can be correctly described using a molecular orbital approach. Besides, it is important to note that one important problem associated with the cluster model approach concerns the truncation of the bonds on the periphery of the cluster generating uncoupled orbitals called dangling bonds. The atoms at the periphery of the cluster are more poorly described than that of the active site; therefore in an SCF procedure, time is spent improving the distribution of the electronic density on the boundary atoms at the expense of the description of the active site. For these reasons the 10 atom clusters (without embedding) used in the present work cannot give a very accurate description of the corresponding metallic surfaces.

It might be expected that the discrepancy observed between the adsorption of ethylene on the Pt surface and the adsorption on the Ag and Cu surfaces, could be probably due to the different d electron participation in the surface binding as a result of the open shell $3d^9$ structure of Pt compared to the closed shells $4d^{10}$ and $3d^{10}$ of silver and copper respectively. The silver and copper d shells are fully occupied and must therefore participate much less in the bonding than the platinum d shells, which are not fully occupied. However, most likely due to the relatively small size of the clusters used (and the consequent problem of the dangling bonds), the analysis of the electronic populations of the metal atoms does not allow us to explain the observed differences in the adsorption energies between the different metals.

However, it is still our belief that the results presented in this work support the usefulness of the cluster model approach in the study of chemical processes on solid surfaces and give new insights in the chemisorption of ethylene on (110) metal surfaces.

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