A bonding study of cyclopentene (c-C$_5$H$_8$) adsorption on Ni(1 1 1) surface

E. Germán, I. López-Corral, A. Juan, G. Brizuela*

Departamento de Física, Universidad Nacional del Sur, Av. Alem 1253, 8000 Bahía Blanca, Argentina

ARTICLE INFO

ABSTRACT

The adsorption of cyclopentene (c-C$_5$H$_8$) on Ni(1 1 1) was studied using DFT and semiempirical calculations. Preferred site and geometry calculations were carried out considering a Ni(1 1 1) surface and a unit cell of 64-atoms. The tetrahedral threefold hollow position was identified as the most favorable site, with a surface-molecule minimum distance of 1.83 Å. A bending structure is adopted when the molecule is adsorbed where the carbon atoms of the double bond are closer to the surface forming an angle of 160° among non-equivalents carbon atoms. The metal surface was represented by a two-dimensional slab with an overlayer of c-C$_5$H$_8$/Ni of 1/9 ratio. We also computed the density of states (DOS) and the crystal orbital overlap populations (COOP) corresponding to C—C, C—Ni, C—H, and Ni—Ni bonds. We found that both Ni—Ni bonds interacting with the ring, and the C=C bond are weakened after adsorption, this last bond is linked significantly to the surface. The hydrogen atoms belonging to the saturated carbon atoms also participate in the adsorbate–surface bonding. The main interactions include the 4s, 3p$_z$ and 5d$_{z^2}$ bands of nickel and 2p$_z$ bands of the carbon atoms of the double bond.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

The study of molecules adsorbed on nickel surfaces is important from both a practical and theoretical point of view and it allows understand the chemical processes associated to the heterogeneous catalysis. Adsorption of hydrocarbons on transition metals has been widely studied due to its usefulness in catalytic processes of industrial relevance. In particular nickel catalysis has found widespread application in hydrocarbon hydrogenation processes over the past several decades [1–4].

The chemisorption implicates a substantial change over electronic density between substrate and catalyst, bonds with intermediate nature between ionic and covalent are established. In particular, the catalytic chemistry study of C$_5$ cycles and intermediates on heterogeneous catalysts has special interest for naphtha reforming [5]. Comelli et al. [6] analyzed the preferred adsorption site and geometry of cyclopentane, cyclopentene and cyclopentadienyl anion on Ni(1 0 0) and Ni(1 1 1) using the extended Hückel Molecular Orbital Method (EHMO) and Becker et al. [7] published a very interesting experimental and theoretical determination of the adsorption site of cyclopentene on Pt and PtSn alloys. Recently Simonetti et al. [8] published a bonding study of c-C$_5$H$_8$ adsorption on the Pt(1 1 1) surface. In preliminary theoretical studies, Brizuela et al. have investigated the adsorption of C$_5$H$_n$ (n = 10, 8 and 5) rings on Pt(1 1 1) [9–12].

The objective of this work is model the adsorption of cyclopentene (c-C$_5$H$_8$) on Ni(1 1 1) surface using a DFT methodology and to study the electronic structure and bonding using a semiempirical qualitative method.

2. The adsorption model and the computational methods

The adsorption geometry was determinate using the ADF program. Gradient-corrected density functional theory (GC-DFT) calculations were performed on a supercell containing 64 atomic sites in a cubic FCC lattice to model the Ni surface by a two-dimensional slab of finite thickness, so as to better simulate the semi-infinite nature of the metallic surface. A four-layer slab was employed as a compromise between computational economy and reasonable accuracy. The molecule was adsorbed on one side of the slab with a 4 × 4 × 4 reciprocal space grid in the supercell Brillouin zone and a plane-wave kinetic energy cutoff of 220 eV for the Ni—C—H [13–15]. We used the Amsterdam Density Functional 2000 package (ADF-BAND2000) [16]. The molecular orbitals were represented as linear combinations of Slater functions. We used the gradient correction approximation of Becke [17] for the exchange energy functional and the B3LYP [18] approximation for the correlation functional. In order to increase the computational efficiency, the innermost atomic shells of electrons are kept frozen for every atom except hydrogen, since the internal electrons do not contribute significantly to the bonding. We used a triple-zeta

* Corresponding author. Tel.: +54 291 4595142; fax: +54 291 4595142.
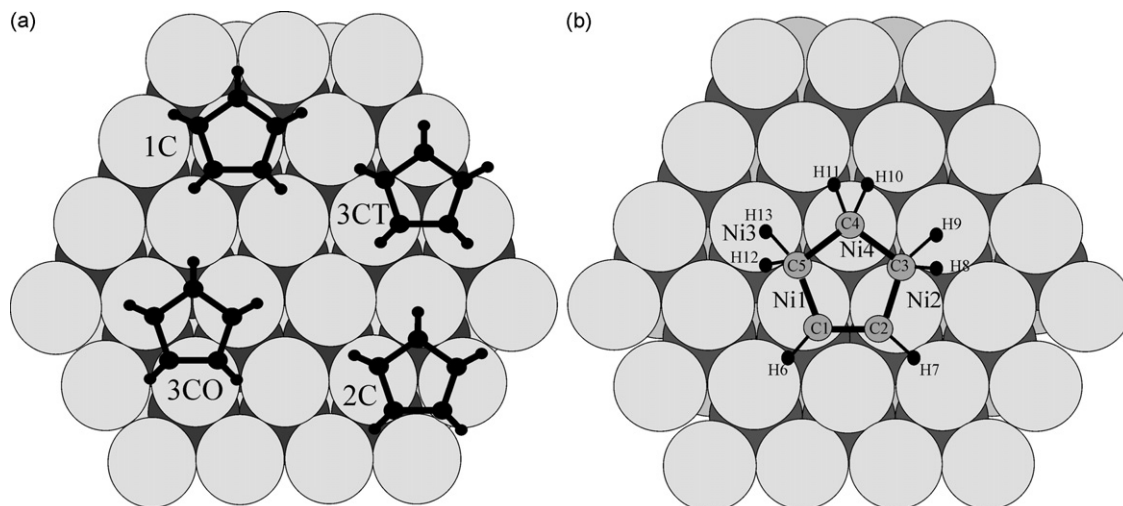*E-mail address:* gbrizuela@uns.edu.ar (G. Brizuela).

Fig. 1. (a) Adsorption sites on the Ni(1 1 1) surface. (b) Preferred adsorption site of cyclopentene on Ni(1 1 1) surface (three coordinated hollow 3-1).

basis set (this means three Slater-type functions for each atomic valence orbital occupied) with polarization functions to express the atomic orbitals of Ni. The basis set of Ni consisted of 3p-, 3d- and 4s-orbitals. The k-points set were generated according to the geometrical method of Ramirez and Böhm [19,20].

The adsorption energies have been calculated with the following total energy difference:

$$\Delta E_{ads} = E(C_5H_8/Ni) - E(C_5H_8) - E(Ni)$$

where $E(C_5H_8/Ni)$, $E(C_5H_8)$ and $E(Ni)$ are the molecular energy on the slab, the molecular energy and the bare slab energy, respectively [9].

The bonding study was performed using the extended Hückel tight binding (EHTB) method, an approximate molecular orbital scheme, implemented with the YAeHMOP package [21]. This method captures efficiently the essential orbital interactions.

The density of states (DOS) of both c-C_5H_8 and Ni surface and the crystal orbital overlap population (COOP) curves between atoms and orbitals were calculated in order to analyze the adsorbate–substrate interactions. The DOS curve is a plot of number of orbitals per unit volume per unit energy. The COOP curve is a plot of the overlap population weighted DOS versus energy. Integration of the COOP curve up to the Fermi level (E_F) gives the total overlap population of the bond specified [22]. Looking at the COOP, we may analyze the extent to which specific states contribute to a bond between atoms or orbitals. The overlap population (OP) shows the degree of bonding of two specified atoms. A positive number means a bonding interaction, while a negative number means an antibonding interaction. When computing the DOS and COOP the system is divided into two fragments, consisting of the surface and adsorbate, respectively. This enables us to compare the changes between the bare surface, the adsorbate, and the composite adsorbed system [23]. Integration of the COOP curve up to the Fermi level gives the total OP.

Henn et al. [24] studying the adsorption of c-C_5H_8 with X-ray photoelectron spectroscopy (XPS), found that approximately four Pt atoms were required to accommodate one molecule. According to XPS results, the maximum absolute coverage of c-$C_5H_5^-$ that could be produced from a single heating of adsorbed c-C_5H_8 was 0.140 ± 0.012. This value is in agreement with the one proposed earlier by Avery for saturation coverage of c-$C_5H_5^-$ on Pt(1 1 1). Even though there is no low energy electron diffraction (LEED)

determination of the surface structure, considering the coverage values estimated by Avery [25] and Henn et al. [24] and our previous theoretical work [26], we decided to adopt a Ni (3×3) surface structure. Our calculations indicate that for this coverage there is no adsorbate–adsorbate repulsion. According to Ref. [25] the experimental coverage is controlled by the Van der Waals interaction between the adsorbates. The adsorption phenomena may involve mainly one, two or more metallic atoms, and according to this choice we can consider four adsorption sites: on top, bridge, hollow octahedral three coordinated (3-3) and hollow tetrahedral three coordinated (3-1) sites. The initial atomic coordinates for the adsorbate was obtained from previous theoretical studies [7,8,12,27,28].

3. Results and discussion

The electronic structure of the c-C_5H_8 molecule can be described taking into account 15 valence orbitals, 14 of them normally occupied. All the occupied molecular orbitals are of closed-shell structure. The interactions between metal atoms and bonded ligands occur mainly through the frontier orbitals of both components. These orbitals for planar c-C_5H_8 are 13a (HOMO−1), 14a (HOMO) and 15a (LUMO), in order of increasing energy.

The molecule-surface distance was optimized to get the minimum total energy and hence to establish the site preference
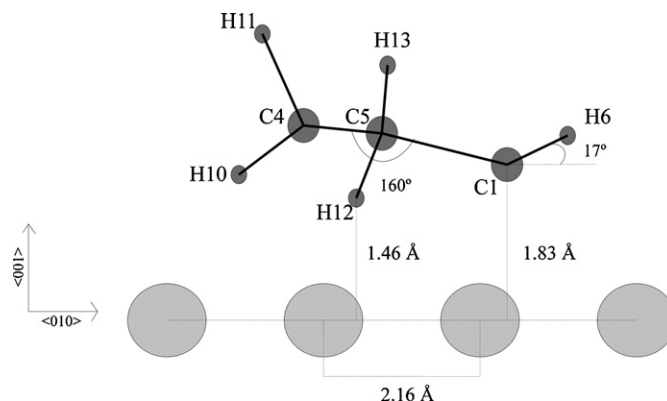

Fig. 2. Side view of C_5H_8 geometry after adsorption.

Table 1
Orbital electron occupations and net charges

	$C_5H_8/Ni(1\,1\,1)$	Isolated C_5H_8
Occupation of HOMO−1	3.797	4
Occupation of HOMO	1.181	2
Occupation of LUMO	0.347	0
Occupation of LUMO+1	0.010	0
Net charge on C_5H_8 unit	1.142	0

between the four different sites for Ni(1 1 1) shown in Fig. 1(a). We started with the c-C_5H_8 geometry reported in Simonetti et al. [8]. The preferred site for the adsorption of cyclopentene on Ni(1 1 1) was the tetrahedral three coordinated (hollow 3-1) as shown in Fig. 1(b). A side view of the adsorption geometry is shown in Fig. 2.

The molecule-surface equilibrium distance is 1.83 Å measured from the C1−C2 double bond (see Fig. 1(b) and Fig. 2). This distance is similar to that of cyclopentadienyl anion-Ni(1 1 1) surface reported in a previous work [29].

The adsorbate state, with the carbon atoms (C=C) is closer to the metallic surface than the rest of the carbon ring, forms an angle of 160° between C1, C5 and C4 as indicated in Fig. 2. This adsorption geometry locates some hydrogen atoms (H8 and H12) to 1.46 Å from the surface. This value is close to 1.50 Å, which corresponds to the Ni−H bond length average [30–32]. According to this we can expect a non-negligible H-surface metal interaction.

4. The chemisorption system

Considering the bare metal surface, the position of the Fermi level shows that the d band is filled. The dispersion of the s and the p bands (not showed) is much larger than the one of the d band, indicating the much more contracted nature of d orbitals. The width of the d band is approximately 4.0 eV for the bare Ni(1 1 1) surface and 5.0 eV for the bulk (three-dimensional) Ni. These values are in agreement with ab initio and semiempirical results reported in the literature [23,33–35].

The Fermi energy of the whole system moves down because of the finite thickness of the slab and electron transfer between the metal surface and the adsorbate. This fact is confirmed by the net charge on the c-C_5H_8 unit of about 1.142, gained at expenses of the metal surface (see Table 1).

In Fig. 3, the DOS plots for c-C_5H_8/Ni(1 1 1) are shown. At left (Fig. 3(a)) is the DOS of a two-dimensional monolayer of c-C_5H_8,

arranged in the same geometry as the molecules take on the surface. All the molecular orbitals have almost at the same energy levels as they have in the isolated specie. The narrowness of the bands in Fig. 3(a) indicates that there is no adsorbate–adsorbate interaction. Fig. 3(b) shows the whole system after chemisorption of c-C_5H_8 on the Ni(1 1 1) slab. The shaded curve shows the contribution of the states of the chemisorbed molecule. Fig. 3(c) shows the DOS curve of the bare Ni surface slab model. Comparing DOS curves between −25 and 5 eV in Fig. 3(a) and (b), we can see the bands corresponding to c-C_5H_8 spreads out after adsorption due to the interaction between orbitals from the molecule and the surface. The projected DOS of c-C_5H_8 is similar to that reported by Becker et al. [7] in the case of Pt(1 1 1).

4.1. Adsorbate frontier orbitals analysis

More information is obtained when we look at what happens to each molecular orbital of c-C_5H_8 upon adsorption. The contributions to the DOS of each of the c-C_5H_8 frontier orbitals are shown in Fig. 4. The horizontal sticks display the energy of the molecular orbitals in the isolated planar species, from HOMO−3 orbital to LUMO+3 orbital. Curves (a), (b), (c) and (d) belong to HOMO−3, HOMO−2, HOMO−1 and HOMO, respectively. Curves (e), (f), (g) and (h) belong to LUMO, LUMO+1, LUMO+2 and LUMO+3, respectively.

Almost all the molecular orbitals of c-C_5H_8 interact with the metal surface, except those lying lower in energy. After adsorption, the whole HOMO band is spread over ca. 7 eV and approach 30% of its DOS is pushed up above the Fermi level. The inner orbitals are spread over approximately 5 eV. The LUMO is spread over 10 eV and the other fragment molecular orbital (FMO) also interacts significantly. We can see clearly the dispersion corresponding to the bands, these are due to the strong interaction with the Ni surface. Using organometallic chemistry language, this means that significant forward-donation from c-C_5H_8 to the surface has occurred. The HOMO band is depopulated by 41% while the LUMO band is pushed up and becomes 18% occupied. This last interaction is the surface counterpart of metal to ligand back-donation. Table 1 contains the main frontier orbitals electronic occupation and resulting net charge for isolated and adsorbed cyclopentene. The more visible effects are the HOMO electronic depopulation and partial LUMO electronic occupation after chemisorption, initially empty for the isolated molecule. As said before, the c-C_5H_8 interacts very strongly with this surface.
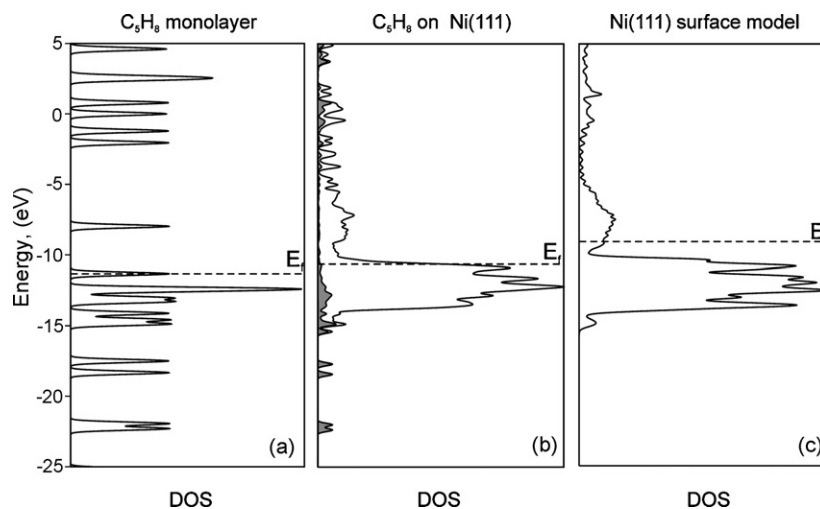

Fig. 3. (a) Total DOS of a monolayer of c-C_5H_8. (b) Total DOS of c-C_5H_8 on Ni(1 1 1). (c) Total DOS of bare Ni(1 1 1) surface.
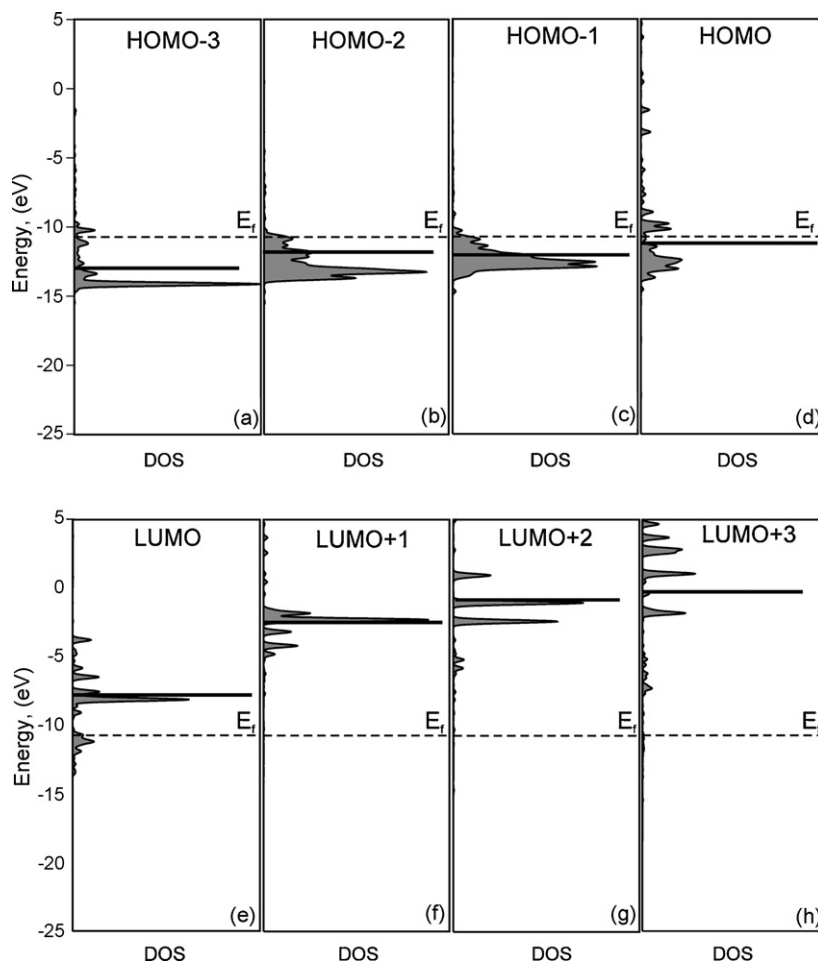
Fig. 4. Frontier orbitals contribution to DOS curves of adsorbed c-C_5H_8.

4.2. Bonding analysis

This analysis was carried out mainly through the OP values for selected bonds (collected in Table 2 and as numbered in Fig. 1). Analyzing the data, we can clearly see, that c-C_5H_8 is adsorbed to the surface bonded mainly by its olefinic carbons. The OP value of the C1—C2 double bond decrease approximately 20% after adsorption, indicative of a weakening of the olefinic C—C bonds that interacts directly with two Ni atoms. The OP for other C—C bonds, C3—C4 or C3—C2, does not change significantly (less than 3%).

The strong adsorbate–surface bonding requires that both C=C and Ni—Ni intrinsic bonding strength decrease. This behavior was also found in the adsorption of benzene and other unsaturated hydrocarbons on Ni(1 1 1) and Pt(1 1 1) [10,36–38]. The Ni1—Ni2 (or Ni1—Ni4) surface bonds are weakened 38% approximately.

The —C—H bonds are also modified during adsorption. In the case of C3—H8 and C5—H12 bonds the OP values decrease approximately 24% and for C4—H10 bond 17%.

The C1—Ni1 and H12—Ni3 interactions have 0.356 and 0.303 OP values, respectively and there is also a bond between C4—Ni4 (0.104), H10—Ni4 (0.122) and a small bond between C5 and Ni1

Table 2
Overlap populations

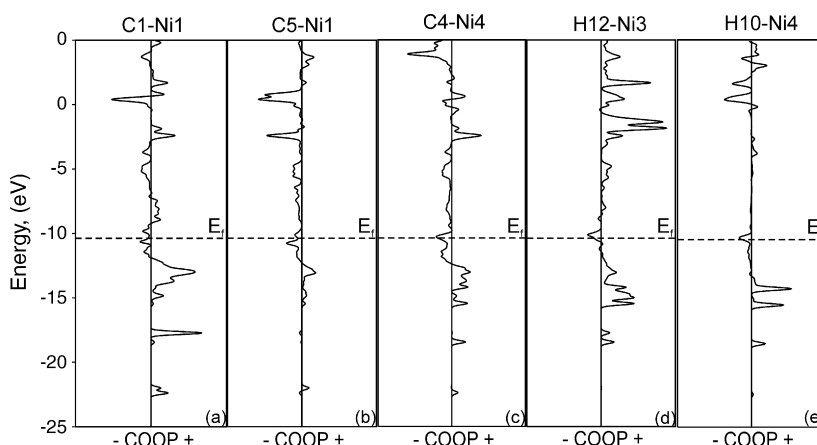| Bond	C_5H_8/Ni(1 1 1)	C_5H_8 monolayer	Surface Ni	Inner Ni	Bulk Ni
C1—C2	0.971	1.208			
C4—H10	0.629	0.758			
C5—H12	0.577	0.758			
C4—C5	0.704	0.685			
C1—H6	0.751	0.755			
Ni1—Ni2	0.144		0.234	0.170	0.148
Ni1—Ni4	0.142		0.221	0.160	
C1—Ni1	0.356				
C5—Ni1	0.012				
C4—Ni4	0.104				
H13—Ni3	0.303				
H10—Ni4	0.122				
Fermi level (eV)	−10.38	−11.31	−10.42		−10.28

Fig. 5. COOP curves for selected bonds. (a) C1—Ni1 bond. (b) C5—Ni1 bond. (c) C4—Ni4 bond. (d) H12—Ni3 bond. (e) H10—Ni4 bond.

(0.012). The interaction of H12 and H10 with Ni3 and Ni4 could be the starting point for a dehydrogenation to a stable $C_5H_5{}^-$ intermediary [29].

The COOP curves for: C1—Ni1, C5—Ni1, C4—Ni4, H12—Ni3 and H10—Ni4 are shown in Fig. 5. The contributions to the right of the vertical axis are bonding between the specified atoms, and to the left are antibonding. The C—Ni COOP curves present two sharp peaks below the Fermi level (between −25 and −15 eV) corresponding to the s orbitals of c-C_5H_8 interacting with the surface. Above −15 eV a broad region comes from the d bands of the Ni surface. We can also notice that H12—Ni3 and C1—Ni1 (and its symmetricals) are the stronger bonds because the COOP curves present only bonding contributions. The C1—Ni1 curves clearly shown the effect of the geometrical and orbitals rearrangements in the C=C bond after adsorption.

4.3. Orbital by orbital contribution to the bonds

To obtain further information about the adsorbate–surface interaction, we studied the contribution to chemisorption of the individual atomic orbitals of the H, C and Ni atoms. The corresponding atomic orbital occupations are displayed in Table 3. We can see a decrease of Ni1, Ni3 and Ni4 d_{z^2} orbitals OP values and Ni1 and Ni4s and p_z orbitals OP after c-C_5H_8 adsorption. Fig. 6 confirm

this behavior, where d_{z^2} and p_z orbitals contributions to total DOS of Ni1, Ni3 and Ni4 are also shown. We must emphasize that d_{z^2} band spreads out above Fermi level after adsorption and intensity p_z orbital band diminishes due its participation in adsorption process. Analyzing the results in Table 3 we can see that the adsorbate p_z orbital, perpendicular to the metal participates in the adsorption on the surface. Its OP value decrease approximately 18% in the case of atoms olefinic carbons, 15% for the saturated carbons (C3 and C5) and 8% for C4.

For C1—Ni1 it can be seen that the bond is mainly due to overlaps between p_z orbital of C and the s, p_z and d_{z^2} orbitals of the metal and that p_z and d_{z^2} contribute more than the s orbital. This is in agreement with the expectation that the p_z orbitals of the carbon ring are important participant in the frontier molecular orbitals [10]. Also, the C p_z orbitals are more developed than other orbitals. The lobes of these orbitals are well oriented to overlap with the metal s and specially with p_z and d_{z^2} metal orbitals. The hydrogen atoms (H8, H10 and H12) bind with the Ni s orbitals.

Finally, Table 4 collects selected OP values between orbitals. The most significant interactions are: C1 $2p_z$–Ni1 4s, C1 $2p_z$–Ni1 $3d_{z^2}$, C1 2s–Ni1 4s, C1 2s–Ni1 $3p_z$, C1 2s–Ni1 $3d_{z^2}$, H12 1s–Ni3 4s, H12 1s–Ni3 $3p_z$, H12 1s–Ni3 $3d_{z^2}$, H10 1s–Ni4 4s.

One of the most important finding of this work is the characterization of the H12—Ni3 bond. The corresponding C—H OP (C5—H12)

Table 3
Atomic orbital occupations for the C_5H_8/Ni chemisorption system

	s	p_x	p_y	p_z	$d_{x^2-y^2}$	d_{z^2}	d_{xy}	d_{xz}	d_{yz}
Ni[a]	0.686	0.146	0.163	0.127	1.652	1.887	1.703	1.888	1.897
Ni1[b]	0.574	0.117	0.116	0.116	1.630	1.618	1.748	1.814	1.849
Ni4[b]	0.520	0.090	0.124	0.093	1.617	1.552	1.753	1.920	1.843
Ni3[b]	0.600	0.125	0.151	0.156	1.657	1.573	1.747	1.863	1.883
C1[a]	1.234	0.928	0.898	0.999					
C1[b]	1.229	0.903	0.877	0.818					
C3[a]	1.216	0.920	0.911	0.905					
C3[b]	1.232	0.858	0.894	0.763					
C4[a]	1.218	0.937	0.911	0.914					
C4[b]	1.224	0.936	0.910	0.837					
H6[a]	0.976								
H6[b]	0.983								
H12[a]	1.006								
H12[b]	0.928								
H10[a]	1.006								
H10[b]	0.929								

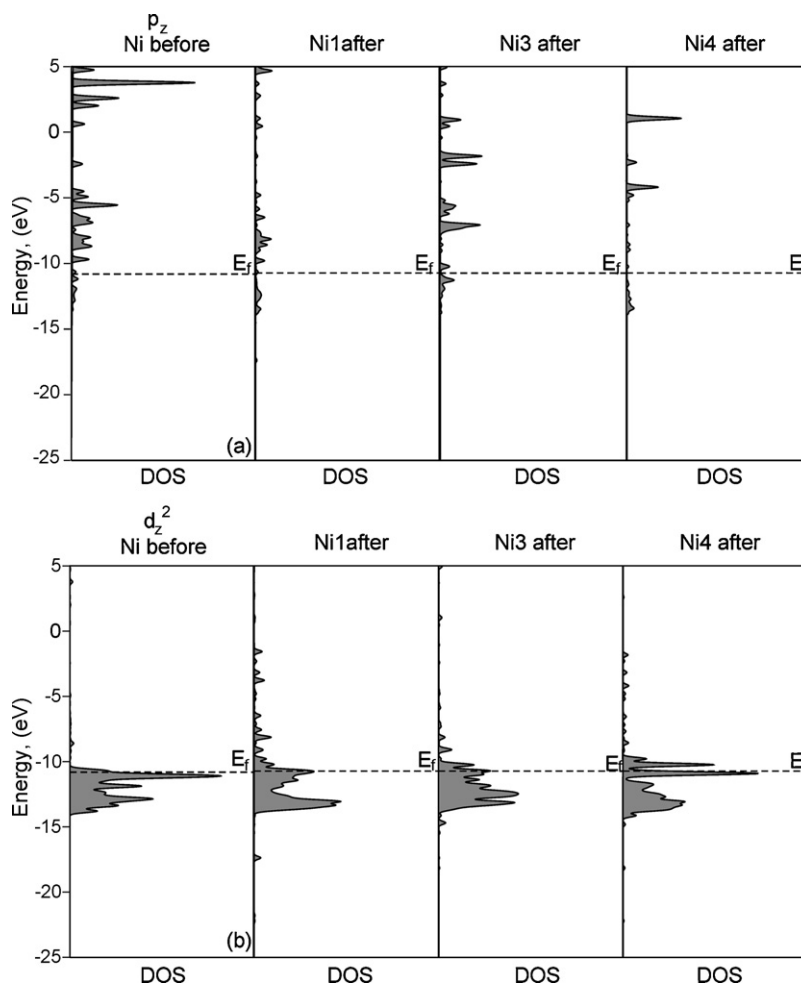[a] Before adsorption.
[b] After adsorption.

Fig. 6. Nickel orbitals contributions to DOS before and after adsorption. (a) p_z orbital contribution. (b) d_{z^2} orbital contribution.

Table 4
Selected overlap populations between C and Ni orbitals and H and Ni orbitals

	C1—Ni1		C1—Ni1		H12—Ni3	H10—Ni4
C2p$_z$ and Ni4s	0.085	C2s and Ni4s	0.053	H1s and Ni4s	0.136	0.058
C2p$_z$ and Ni3p$_x$	0.006	C2s and Ni3px	0.003	H1s and Ni3px	0.002	0.000
C2p$_z$ and Ni3p$_y$	0.002	C2s and Ni3py	0.000	H1s and Ni3py	0.003	0.018
C2p$_z$ and Ni3p$_z$	0.023	C2s and Ni3pz	0.026	H1s and Ni3pz	0.080	0.022
C2p$_z$ and Ni3d$_{x^2-y^2}$	0.000	C2s and Ni3d$_{x^2-y^2}$	0.000	H1s and Ni3d$_{x^2-y^2}$	0.000	0.004
C2p$_z$ and Ni3d$_{z^2}$	0.086	C2s and Ni3d$_{z^2}$	0.019	H1s and Ni3d$_{z^2}$	0.058	0.002
C2p$_z$ and Ni3d$_{xy}$	0.000	C2s and Ni3d$_{xy}$	0.000	H1s and Ni3d$_{xy}$	0.000	0.000
C2p$_z$ and Ni3d$_{xz}$	0.030	C2s and Ni3d$_{xz}$	0.005	H1s and Ni3d$_{xz}$	0.014	0.000
C2p$_z$ and Ni3d$_{yz}$	0.009	C2s and Ni3d$_{yz}$	0.001	H1s and Ni3d$_{yz}$	0.010	0.017

decreases from 0.758 to 0.577, after adsorption (24%) that is the higher change in the molecule. At the same time, the H—Ni bond is formed (OP 0.303). The composition of this bond is shown in Table 4. The major contributions are H 1s–Ni 4s and H 1s–Ni 3p$_z$. In a memorable work, Saillard and Hoffmann have described the bonding of cyclic or chain alkenes chemisorption proceeding by a variety of surface-H contacts [39].

Becker et al. have described a new loss peak at 341 meV in the HREEL of a monolayer of c-C_5H_8 on Pt, which they have assigned to a softened C—H stretching mode coming from a hydrogen bonded to the metal surface. Their computed geometry by DFT calculation predict a Pt—H bond [7]. We have found this bond and described its COOP curves for Pt—Pt in Simonetti et al. [8]. Our present findings in the case of Ni confirm this behavior in another metal.

5. Conclusions

In this work we have analyzed the electronic structure changes and bonds formations during c-C_5H_8 adsorption on Ni(1 1 1) surface, by means of DFT and semiempirical qualitative theoretical calculations. The molecule binds to the surface in a three coordinated (hollow 3-1) site, 1.83 Å away from metallic surface, bonding mainly through unsaturated carbons and hydrogens atoms belonging to the saturated carbons. A bend angle of 160° between C1, C4 and C5 carbons was found. A decrease in the C=C, C—H and Ni—Ni bonds strength were observed, and the formation of =C—Ni and H—Ni bonds formation was detected, describing the basic interactions during chemisorption. We also found that Ni s, p$_z$ and d$_{z^2}$ orbitals, C s and p$_z$ orbitals (normal to the surface) and H s orbital

play an important role in the bonding between c-C_5H_8 and the surface.

References

[1] V.I. Filippov, W. Moritz, A.A. Terentjev, A.A. Vasiliev, S.S. Yakimov, IEEE Sens. J. 7 (2007) 192.
[2] W.J. Lee, C.Z. Li, Appl. Catal. A: Gen. 316 (2007) 90.
[3] Y.H. Chin, D.L. King, H.S. Roh, Y. Wang, S.M. Heald, J. Catal. 244 (2006) 153.
[4] F. Zaera, Top. Catal. 34 (2005) 129.
[5] V. Haensel, M.J. Sterba, Progress in Petroleum Technology, Adv. Chem. Ser. 5, 1951, p. 60.
[6] N.C. Comelli, M.B. López, E.A. Castro, J. Mol. Struct. Theochem. 726 (2005) 197.
[7] C. Becker, F. Delbecq, J. Breitbach, G. Hamm, D. Franke, F. Jäger, K. Wandelt, J. Phys. Chem. B 108 (2004) 18960.
[8] S. Simonetti, P. Jasen, E. Gonzalez, A. Juan, G. Brizuela, Appl. Surf. Sci. 252 (2006) 7515.
[9] G. Brizuela, N.J. Castellani, Surf. Sci. 401 (1998) 297.
[10] G. Brizuela, R. Hoffmann, J. Phys. Chem. A 102 (1998) 9618.
[11] G. Brizuela, N.J. Castellani, Surf. Sci. 411 (1998) 154.
[12] G. Brizuela, N.J. Castellani, J. Mol. Catal. A: Chem. 139 (1999) 209.
[13] P. Hohenberg, W. Kohn, Phys. Rev. 136 (1964) 864.
[14] W. Koh, L.J. Sham, Phys. Rev. 140 (1965) 1133.
[15] R.G. Parr, W. Yang, Density Functional Theory of Atoms and Molecules, Oxford University Press, New York, 1989.
[16] Amsterdam Density Functional Package Release 2001, Vrije Universiteit, Amsterdam.
[17] D. Becke, Phys. Rev. A 38 (1988) 3098.
[18] C. Lee, W. Yang, R.G. Parr, Phys. Rev. B 37 (1988) 785.
[19] R. Ramirez, M.C. Böhm, Int. J. Quantum Chem. 30 (1986) 391.
[20] R. Ramirez, M.C. Böhm, Int. J. Quantum Chem. 34 (1988) 571.
[21] G. Landrum, W. Glassey, Yet Another extended Hückel Molecular Orbital Package (YAeHMOP), Cornell University, 2004, available at http://sourceforge.net/projects/yaehmop/.
[22] R. Hoffmann, Solids and Surfaces: A Chemist's View of Bonding in Extended Structures, VCH, New York, 1988.
[23] A.W. Edith Chan, R. Hoffmann, J. Chem. Phys. 92 (1) (1990).
[24] F. Henn, P.J. Dalton, C.T.J. Campbell, Phys. Chem. 93 (1989) 836.
[25] N.R. Avery, Surf. Sci. 146 (1984) 363.
[26] G. Brizuela, N.J. Castellani, Surf. Sci. 408 (1998) 537.
[27] S. Simonetti, G. Brizuela, Int. J. Chem. React. Eng. 3 (2005).
[28] W.L. Manner, G.S. Girolami, R.G. Nuzzo, J. Phys. Chem. B 102 (1998) 10295.
[29] E. Germán, S. Simonetti, M. Pronsato, A. Juan, G. Brizuela, Appl. Surf. Sci. (2008), doi:10.1016/j.apsusc.2008.03.061.
[30] D.J. Klinke, L.J. Broadbelt, Surf. Sci. 429 (1999) 169.
[31] M.B. Jensen, U. Olsbye, O. Swing, Chem. Phys. Lett. 432 (2006) 94.
[32] R.T. Vang, K. Honkala, S. Dahl, Surf. Sci. 600 (2006) 66.
[33] A.I. Lichtenstein, M.I. Katsnelson, Phys. Rev. Lett. 87 (4) (2001) 067205.
[34] Y.-T. Wong, R. Hoffmann, J. Chem. Soc., Faraday Trans. 86 (24) (1990) 4083.
[35] S.-S. Sung, R. Hoffmann, J. Phys. Chem. 90 (1986) 1380.
[36] F. Mittendorfer, J. Hafner, Surf. Sci. 472 (2001) 133.
[37] C. Minot, M.A. Van Hove, G.A. Somorjai, Surf. Rev. Lett. 2/3 (1995) 285.
[38] J. Silvestre, R. Hoffmann, Langmuir 1 (1985) 621.
[39] J.-Y. Saillard, R. Hoffmann, J. Am. Chem. Soc. 106 (1984) 2006–2026.