c-C$_5$H$_5$ on a Ni(1 1 1) surface: Theoretical study of the adsorption, electronic structure and bonding

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ABSTRACT

In the present work the ASED-MO method is applied to study the adsorption of cyclopentadienyl anion on a Ni(1 1 1) surface. The adsorption with the centre of the aromatic ring placed above the hollow position has been identified to be energetically the most favourable. The aromatic ring remains almost flat, the H atoms are tilted 17° away from the metal surface. We modelled the metal surface by a two-dimensional slab of finite thickness, with an overlayer of c-C$_5$H$_5$$^-$, one c-C$_5H_5$$^-$ per nine surface Ni atoms. The c-C$_5$H$_5$$^-$ molecule is attached to the surface with its five C atoms bonding mainly with three Ni atoms. The Ni–Ni bond in the underlying surface and the C–C bonds of c-C$_5$H$_5$$^-$ are weakened upon adsorption. We found that the band of Ni 5d$_{z^2}$ orbitals plays an important role in the bonding between c-C$_5$H$_5$$^-$ and the surface, as do the Ni 6s and 6p$_z$ bands.

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1. Introduction

The chemisorption of molecules on metallic surfaces is important from the point of view of the molecular structure and it allows to understand the chemical processes associated with the heterogeneous catalysis [1,2]. The interaction of alkanes with metal surfaces has received considerable study in the surface science community. In particular nickel catalysis has found widespread application in hydrocarbon hydrogenation processes over the past several decades [3]. Understanding the preferred orientation and bonding of alkanes to surfaces is clearly important for further elucidation of reaction potential energy surfaces [4]. During hydrocarbon conversion reactions the breaking of H–H, C–H and C–C bonds are essential processes. It has been recognized that isomerization and dehydrocyclization reactions of C$_6$ paraffins have both the same intermediate of C$_5$ cyclic nature [5–7]. Especially interesting is the work of Gault [5] on methylcyclopentane hydrogenolysis, where different products are obtained depending on the C–C bond of the cyclic that is broken.

The adsorption of cyclopentadienyl anion on Pt(1 1 1) was originally considered by Avery [8–11] employing the thermal desorption spectroscopy (TDS), electron energy loss spectroscopy (EELS) and work function changes (WFCs) techniques. Recently,

Comelli et al. [12] 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).

There are several experimental works devoted to the experimental characterization of cyclic hydrocarbons on transition metals, but theoretical studies are scarce and mainly focused on the adsorption of benzene [13–17]. In previous works we have studied the adsorption of C$_5$ cycles on Pt(1 1 1) [6,18–21].

The objective of this work is to study the adsorption of cyclopentadienyl anion on a Ni(1 1 1) metal surface, including repulsive terms to the energy. After finding the optimum geometry of the molecule we analyze the electronic structure and bonding.

2. Theoretical method and adsorption model

The molecular orbital calculations performed in the present work are based on the atom superposition and electron delocalization (ASED) method [22]. In this quantum chemical technique an extended Hückel (EH)-like Hamiltonian is used for the calculation of valence electron eigen-energies [23,24]. The main modification is the substitution of the Wolfsberg–Helmholtz constant for off-diagonal elements by a distance-dependent expression. In addition, a pairwise repulsive term is included to take into account the repulsive interaction between screened cores, allowing the determination of equilibrium geometries for the adsorbed species. This formulation can be rationalized by applying the Hellmann–Feynman theorem [22].

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Table 1
Extended Hückel parameters

Atom	Orbital	VSIP (eV)	ζ_1	ζ_2	C_1	C_2
H	1s	−12.60	1.20			
C	2s	−19.00	1.658			
	2p	−10.26	1.618			
Ni	4s	−9.635	1.80			
	4p	−5.990	1.50			
	3d	−12.00	5.75	2.00	0.5683	0.6292

The atomic parameters (ionization potentials: IPs and Slater exponent of atomic orbitals) employed have been detailed in Table 1.

The interaction between one c-$C_5H_5^-$ single molecule and the Ni(1 1 1) surface was studied within the cluster approach. The Ni(1 1 1) surface was represented by a 64-atom cluster distributed in three layers of 27 (first layer), 19 (second layer) and 18 (third layer) atoms.

Structural parameters and interatomic Ni–Ni distances were taken from Ref. [25]. For the Ni(1 1 1) surface four different sites have been considered: on top, bridge, hollow (3-3) and hollow (3-1) sites [12]. The starting coordinates of the adsorbate were obtained from [6] and from experimental data in nickelocene bared systems [26–31].

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

$$\Delta(E_{ads}) = E(C_5H_5/Ni_{64}) - E(C_5H_5) - E(Ni_{64})$$

where $E(C_5H_5/Ni_{64})$, $E(C_5H_5)$ and $E(Ni_{64})$ are the molecular energy on the cluster, the molecular energy and the bare cluster energy, respectively [6].

The calculations of the electronic structure and bonding were performed using the YAeHMOP package. The programs *bind* and *viewkel* form the core of the package [32]. This method captures well the essential orbital interactions in chemisorption.

In the case of electronic structure calculations, the system was modelled by a two-dimensional slab of finite thickness, so as to better simulate the semi-infinite nature of the metallic surface; based on previous studies of the same molecule adsorbed on a Pt(1 1 1) surface carried out for Brizuela and Hoffmann [21]. The molecule was adsorbed on one side of the slab. It was used a Ni (3×3) surface structure, thus there is not adsorbate–adsorbate repulsion. The cyclopentadienyl anion was assumed to lie with its C_5 ring parallel to the surface [8].

The density of states (DOS) of both c-$C_5H_5^-$ and Ni and the crystal orbital overlap population (COOP) curves between atoms and orbitals were calculated in order to analyze the adsorbate–surface interactions. The overlap population (OP) shows the degree of bonding of two specified atoms. A positive number means a
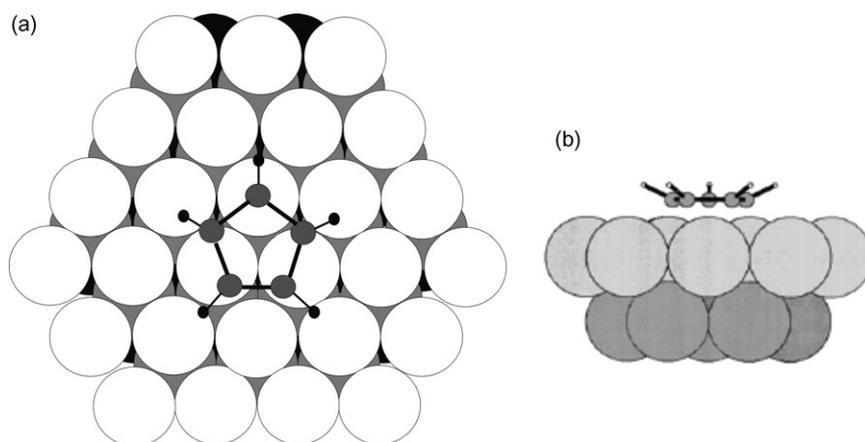

Fig. 1. (a) Preferred adsorption site of cyclopentadienyl anion on Ni(1 1 1) surface, tricoordinate hollow 3-1. (b) Angle C–H of $C_5H_5^-$ after adsorption.
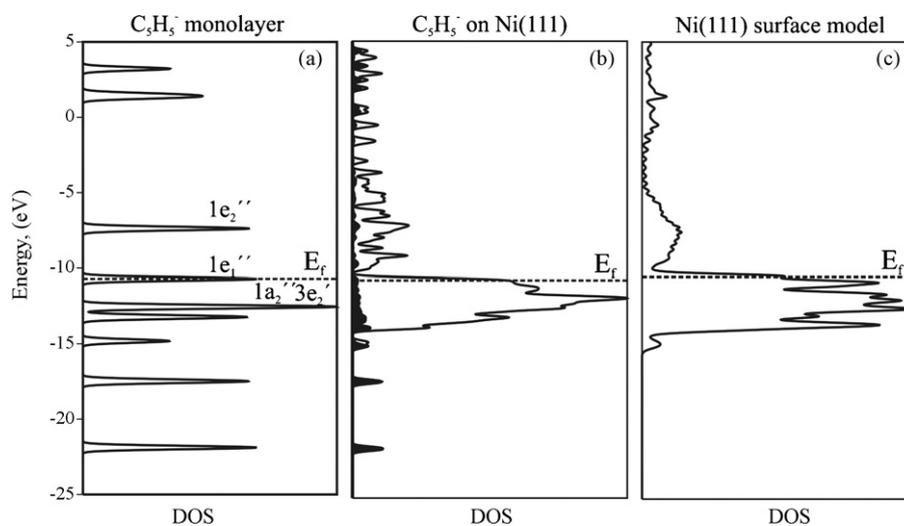

Fig. 2. (a) Total DOS of a monolayer of c-$C_5H_5^-$. (b) Total DOS of c-$C_5H_5^-$ on Ni(1 1 1). (c) Total DOS of bare Ni(1 1 1) surface.

bonding interaction, while a negative number means an anti-bonding interaction. Furthermore, COOP plots tell us the bonding character and the relative bond strength of a certain bond as a function of the energy of the orbitals, weighting the DOS in each energy interval by its contribution to the OP. Our general approach is that of a fragment analysis. The system is divided into two fragments, consisting of the surface and adsorbate, respectively, which are then interacting. This enables us to compare the changes between the bare surface, the adsorbate, and the composite adsorbed system [33]. Integration of the COOP curve up to the Fermi level gives the total OP [34].

The cyclopentadienyl molecule and its substituted derivatives are very important as ligands in transition metal chemistry, leading to stable organometallic complexes. Interactions between metal atoms and bonded ligands occur mainly through the frontier orbitals of both components. These orbitals for c-$C_5H_5^-$ are, in order of increasing energy, $3e_2'$ (a degenerate σ orbital set, doubly occupied), $1a_2''$ (π orbital), $1e_1''$ (degenerate π orbital set, highest occupied) and $1e_2''$ (degenerate π orbital set, unoccupied) [21,35]. The $1e_1''$ and $1e_2''$ bands correspond to the HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) of one molecule, respectively.

We have worked with the cyclopentadienyl anion because it gives us a closed shell description for the $C_5H_5^-$ fragment.

3. Results and discussion

The molecule–surface distance was optimized to get the minimum total energy and hence to establish the site preference. After that, we optimized the angle, the hydrogen atoms form with the ring. In all cases the site of adsorption was placed near the centre of the cluster to avoid undesirable border effects. The adsorption site and the hydrogen angle with the carbon ring are shown in Fig. 1(a) and (b).

The preferred site for the adsorption of cyclopentadienyl on Ni(1 1 1)$_{64}$ is a tricoordinate (hollow 3-1) site and it bonds at an equilibrium distance equal to 1.83 Å, forming C–H angles of 17° away from the metal surface, as displayed in Fig. 1(b). Comelli et al. do not report this bending angle [12]. Nevertheless Jing and Whitten [36] in their theoretical study to the adsorption of benzene on Ni(1 1 1) reported that the C–H bonds present an important bending away angle of 8.5° with respect to the molecular plane. For benzene on Ni(1 1 1) Mittendorfer and Hafner also observed that the hydrogens atoms are tilted 19° away from the surface of the substrate [17]. The two energetically most favourable adsorption positions for the benzene molecule are the hcp hollow and the bridge position, while the C–Ni distances

are 1.93 and 1.92 Å, respectively. On the other hand, Ohtani et al. [37] using low energy electron diffraction (LEED) technique observed the same phenomenon in the case of the benzene adsorbed on Rh(1 1 1). An important bending away angle (20°) has also been reported by Anderson et al. [38] for benzene on Pt(1 1 1). Our group also found a bending angle (26°) for $C_5H_5^-$ on Pt(1 1 1) [6].

Fig. 2 shows (a) the DOS curve of a two-dimensional monolayer of c-$C_5H_5^-$. The narrowness of the bands in (a) indicates that there is no adsorbate–adsorbate interaction. Fig. 2(b) shows the whole system after chemisorption c-$C_5H_5^-$ on Ni(1 1 1) slab. The shaded curve shows the contribution of the states of the chemisorbed molecule. Fig. 2(c) shows the DOS curve of the bare Ni surface slab model. Comparing DOS curves between −25 and 5 eV in Fig. 2(a) and (b), we can see that the bands corresponding to c-$C_5H_5^-$ spread out after adsorption due to the interaction between 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 ($W_d = 4.0$ eV) [33,39–41].

Table 2 collects results of electronic configurations of the surface and bulk (three-dimensional) Ni atoms. The occupation of the valence s orbitals seems to be slightly lower and that of the p orbitals slightly greater that would have been anticipated. The surface-layer of the slab is negatively charged relative to the bulk due to the greater number of interactions [42].

The DOS curves of each of the cyclopentadienyl anion frontier orbitals, after adsorption, are shown in Fig. 3. The horizontal sticks display the energy of the molecular orbitals in the isolated planar species. Curves (c) and (d) belong to the HOMO ($1e_1''$) and LUMO ($1e_2''$), respectively. We can see clearly the dispersion corresponding to the bands, these are due to the strong interaction with the Ni surface. After adsorption the whole $1e_1''$ band is spread over about 18 eV and 38% of its DOS is pushed above the Fermi level. The $1a_2''$ fragment molecular orbital (FMO) (the lowest π orbital of c-$C_5H_5^-$) also interacts substantially, 15% of the DOS is pushed up above the Fermi level and the main body of the band is pushed down about 0.5 eV. Even the σ $3e_2'$ band also interacts because a sharp peak before adsorption is a dispersed band after adsorption. This means

Table 2
Population of Ni orbitals in bulk Ni and the slab model for a Ni surface

	4s	4p	3d	Total
Surface-layer Ni	0.68	0.44	9.03	10.147
Inner-layer Ni	0.61	0.41	8.69	9.704
Bulk Ni	0.51	0.49	9.00	10.00

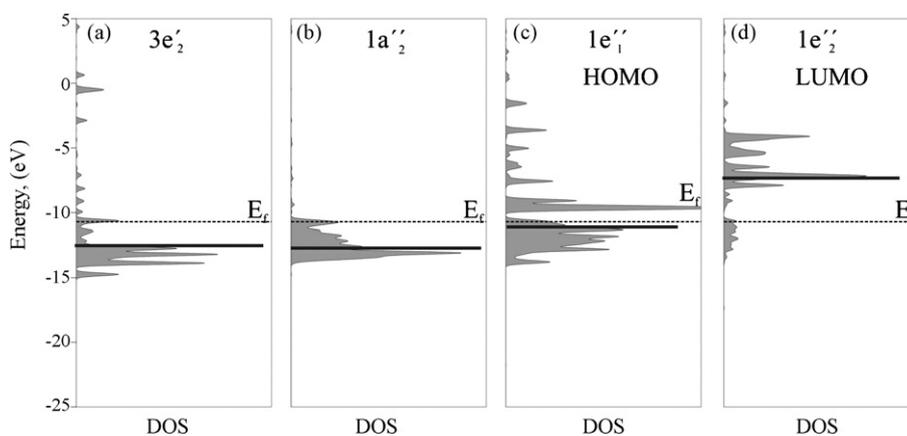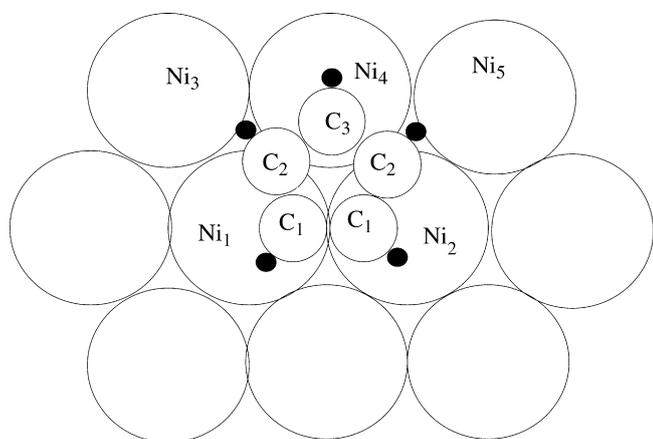**Fig. 3.** Contribution of the frontier orbitals of c-$C_5H_5^-$/Ni(1 1 1). The horizontal solid lines indicate the orbital positions in the isolated planar c-$C_5H_5^-$ molecule.

Table 3
Overlap populations and Fermi levels

Bond	$C_5H_5^-$/ $Ni(1\,1\,1)$	$C_5H_5^-$ monolayer	Surface Ni	Inner Ni	Bulk Ni
C_1–C_2	0.815	0.942			
C_1–C_1	0.836	0.959			
C_2–C_3	0.824	0.948			
C_1–H	0.781	0.775			
C_2–H	0.765	0.774			
C_3–H	0.777	0.775			
Ni–Ni	0.136		0.234	0.170	0.148
Ni_1–Ni_4	0.127		0.233	0.160	
C_1–Ni_1	0.353				
C_3–Ni_4	0.396				
C_2–Ni_1	0.172				
C_2–Ni_3	0.130				
C_2–Ni_4	0.040				
Ni_1–H	−0.036				
Ni_4–H	−0.038				
Ni_3–H	0.028				
Fermi level (eV)	−10.34	−10.70	−10.42		−10.28

Table 4
Orbital electron occupations and net charges

	$C_5H_5^-$/Ni(1 1 1)	Isolated $C_5H_5^-$
Occupation of $3e^{2'}$	3.447	4
Occupation of $1a^{2''}$	1.897	2
Occupation of $1e^{1''}$	2.118	4
Occupation of $1e^{2''}$	0.472	0
Net charge on C_5H_5 unit	0.950	−1

The OP between atoms and the Fermi levels are shown in Table 3 and the numbering of atoms of c-$C_5H_5^-$/Ni(1 1 1) in Fig. 4. The C–C OP decreases approximately 13% after adsorption, indicative of a weakening of the C–C bonds. The C–H bonds do not suffer significant changes. A large bonding OP between C and Ni atoms appears, while the Ni–Ni OP decreases, this indicates that the strong adsorbate–surface bonding requires that C–C and Ni–Ni bonding decrease. The bonds which contribute significantly to the c-$C_5H_5^-$ adsorption are C_1–Ni_1, C_3–Ni_4 and C_2–Ni_1. Although the C_2–Ni_4 distance is shorter than the C_2–Ni_3 distance, the OP of the bond is approximately four times smaller than that of the latter. Thus the cyclopentadienyl anion is adsorbed to the surface bonding mainly to three Ni atoms (Ni_1, Ni_2 and Ni_4).

To study the bonding in details we have plotted the COOP curves for C_1–Ni_1, C_3–Ni_4, C_2–Ni_1 and C_2–Ni_3 bonds in Fig. 5. The contributions to the right of the vertical axis are bonding between the specified atoms, and to the left are antibonding. In the four COOP curves it can be observed two sharp peaks below the Fermi level (between −25 and −15 eV) corresponding to the s orbitals of c-$C_5H_5^-$. Above −15 eV it can be seen a broad region due to d orbitals of Ni surface. In this region there are contributions of $3e_2'$, $1a_2''$, $1e_1''$ and $1e_2''$ frontier orbitals. The bonding can be described as adsorbate $3e_2'$, $1a_2''$ and $1e_1''$ to metal foward-donation as well as metal to $1e_2''$ back-donation. The global result of these interactions is two peaks and a broad region of Ni–C bonding, with a small region of antibonding. The participation of σ orbitals ($3e_2'$ and $3a_1'$) and π orbitals ($1a_2''$, $1e_1''$ and $1e_2''$) is similar to the orbital mixing found for benzene on Ni(1 1 1) [38].

The bending of hydrogen atoms out of the carbon plane is traced to π interactions and reorientation of these orbitals for better overlap in molecular complexes [43]. When c-$C_5H_5^-$ is adsorbed on Pt(1 1 1) and the geometry optimized, also the lowest energy is achieved with a bending of ring hydrogen atoms away from the surface. There is involvement of the σ system of the molecule in bonding to the surface, this shows up in the dispersion and depopulation of $3e_2'$ (see Fig. 3).

Fig. 4. Numbering of atoms of c-$C_5H_5^-$/Ni(1 1 1).

that important foward-donation from c-$C_5H_5^-$ to the surface has occurred. Also the body of the $1e_2''$ band is pushed up and down to the Fermi level and spread over about 19 eV. This fragment molecular orbital becomes about 17% occupied. This is due to the metal to ligand back-donation. Therefore c-$C_5H_5^-$ interacts very strongly with the surface.

Fig. 5. (a) COOP curve for C_1–Ni_1 bond. (b) COOP curve for C_3–Ni_4 bond. (c) COOP curve for C_2–Ni_1 bond. (d) COOP curve for C_2–Ni_3 bond.

Table 5
Atomic orbital occupations for the c-$C_5H_5^-$/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
Ni_1[b]	0.569	0.110	0.137	0.119	1.679	1.554	1.762	1.852	1.747
Ni_3[b]	0.624	0.131	0.153	0.118	1.708	1.855	1.745	1.875	1.886
Ni_4[b]	0.564	0.113	0.123	0.116	1.710	1.490	1.724	1.792	1.872
C[a]	1.231	0.920	0.912	1.173					
C_1[b]	1.228	0.899	0.874	0.866					
C_2[b]	1.233	0.860	0.878	0.818					
C_3[b]	1.225	0.908	0.869	0.895					

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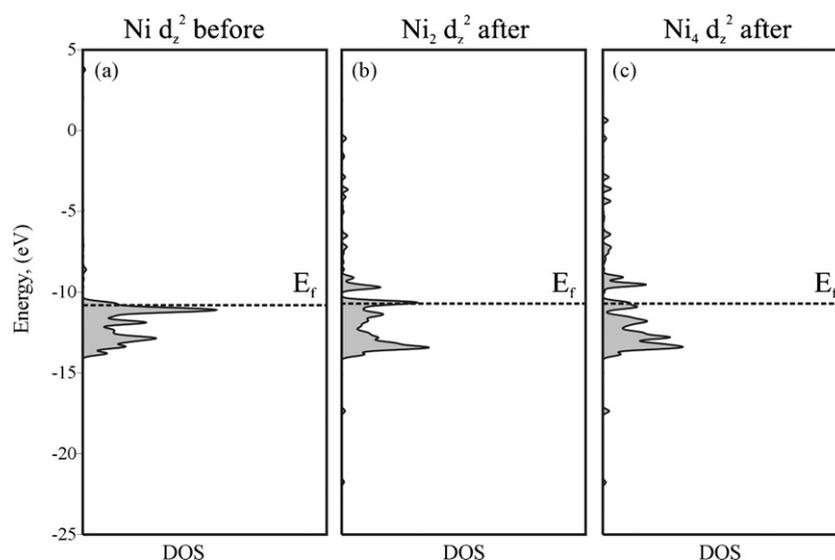[b] After adsorption.

Fig. 6. (a) Contribution of d_{z^2} orbital to DOS of Ni before adsorption. (b) Contribution of d_{z^2} orbital to DOS of Ni_2 after adsorption. (c) Contribution of d_{z^2} orbital to DOS of Ni_4 after adsorption.

In Table 4 the calculated orbital electron occupations for the adsorbed and isolated c-$C_5H_5^-$ and the net charge on the molecule are showed. It can be seen depopulation after adsorption of $1a_2''$ and $3e_2'$ orbitals, while the $1e_2''$ orbital (LUMO), initially empty, is partially occupied, and the $1e_1''$ orbital (HOMO) suffers a significant depopulation. We can also observe an important electron transfer ($\simeq 1.9e^-$) from the molecule to the surface. Hence the foward-donation from $1a_2''$ and $1e_1''$ is greater than the $1e_2''$ back-donation of electrons, so the adsorbed molecule emerges positively charged relative to c-$C_5H_5^-$. Similar charge transfer was reported for c-$C_5H_5^-$ on Pt(1 1 1) and benzene on Pt(1 1 1) using ASED [21,38]. On the other hand, Mittendorfer and Hafner [17] using VASP found for benzene on Ni(1 1 1) that the formation of the chemisorption bond is dominated by donations of electrons from the $d_{3z^2-r^2}$ orbitals of the substrate atoms and, to a lesser extent, from π states of the aromatic ring, into covalent bonds between C and Ni atoms. In addition, back-donation into t_{2g} orbitals of the substrate has been found. Ab initio CI calculations show a slight increase in energy of the Fermi level and a decrease in the energy of the benzene 1s SCF levels, suggesting that the molecule transfers charge to their Ni cluster [36].

We studied the contribution to chemisorption of the individual atomic orbitals of the C and Ni atoms and the data is listed in Table 5. It can be seen that after adsorption both Ni_1 and Ni_4 OP of s, p_x, p_y and d_{z^2} orbitals decrease. The more considerable changes of c-$C_5H_5^-$ occur with p_z orbitals (decrease approximately 25%). The Pt p and C s, p_x and p_z orbitals show only small changes (less than $0.05e^-$). This was also found for c-$C_5H_5^-$ on Pt(1 1 1) [21].

The contribution of the Ni_2 and Ni_4 d_{z^2} orbitals to the total DOS is shown in Fig. 6. We can see clearly that after adsorption the d_{z^2} band spreads out above the Fermi level. Hence we have interactions between the whole d_{z^2} band of both Ni_2, Ni_4 and $3e_2'$, $1a_2''$, $1e_1''$, and $1e_2''$ molecular orbitals of c-$C_5H_5^-$.

Selected OP between C $2p_z$ and Ni orbitals are shown in Table 6 to get more information about adsorbate–surface interaction. For C_3–Ni_4 and C_1–Ni_1 it can be seen that the bond is mainly due to overlaps between the p_z orbital of C and the s, p_z and d_{z^2} orbitals of the Ni surface and that 4s and d_{z^2} contribute more than p_z orbital. The p_z orbitals of the C ring are important participants in the frontier molecular orbitals. The lobes of these orbitals are well oriented to overlap with the metal s, and especially with p_z and d_{z^2} orbitals [21].

Table 6
Selected overlap populations between C and Ni orbitals

	C_1–Ni_1	C_3–Ni_4	C_2–Ni_1	C_2–Ni_3
C $2p_z$ and Ni 4s	0.091	0.103	0.049	0.036
C $2p_z$ and Ni $4p_x$	0.002	0.000	0.000	0.006
C $2p_z$ and Ni $4p_y$	0.005	0.000	0.016	0.004
C $2p_z$ and Ni $4p_z$	0.023	0.029	0.011	0.007
C $2p_z$ and Ni $3d_{x^2-y^2}$	0.000	0.000	0.009	0.000
C $2p_z$ and Ni $3d_{z^2}$	0.080	0.145	0.006	0.000
C $2p_z$ and Ni $3d_{xy}$	0.000	0.000	0.000	0.005
C $2p_z$ and Ni $3d_{xz}$	0.024	0.000	0.000	0.010
C $2p_z$ and Ni $3d_{yz}$	0.024	0.000	0.055	0.008
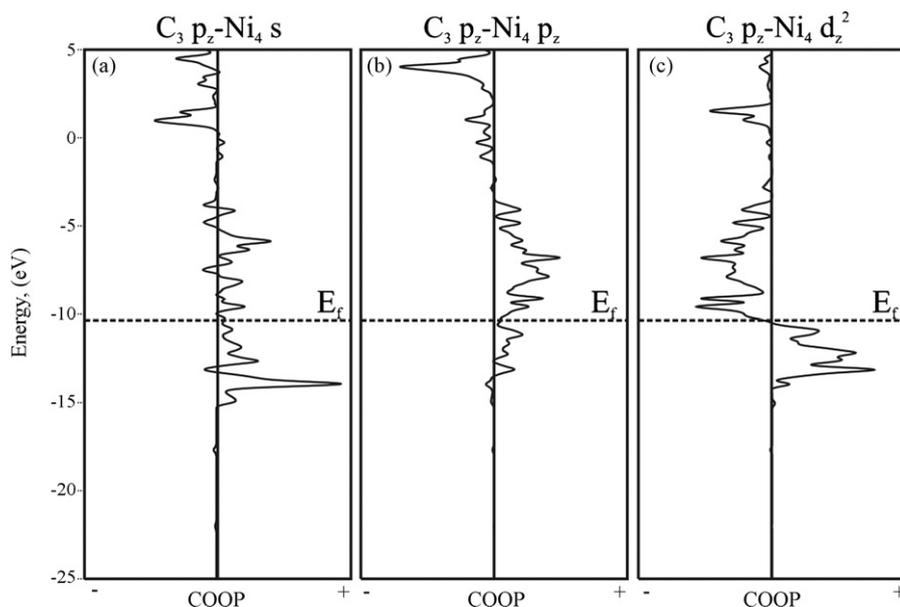
Fig. 7. (a) COOP curve for C_3 p_z–Ni_4 s. (b) COOP curve for C_3 p_z–Ni_4 p_z. (c) COOP curve for C_3 p_z–Ni_4 d_{z^2}.

The more important interactions between orbitals are shown in Fig. 7. We can analyze orbital by orbital contributions to the COOP curves. It can be see that the first and second curves are mostly bonding for energies lower than 0 eV. Above it the three curves are always antibonding. The C_3 p_z–Ni_4 d_{z^2} orbitals are bonding below the Fermi level; above it they are antibonding. This analysis agrees with previous consideration. For example, Fig. 7(a) supports the interpretation that the small peak at $\simeq -15$ eV is due to the interaction between Ni s and Cp_z (see Fig. 5(b)); the next peak at -14 eV is also due to the interaction of Ni s and Cp_z, while the peak at -13 eV is due to the interaction of Ni d_{z^2} and Cp_z.

We can see that not only d orbitals play a significant role in the bonding with the surface, but the contribution of metal s and p orbitals is also important.

In a related study, ab initio calculations for benzene on Ni(1 1 1) have shown an important interaction between benzene π orbitals and Ni 3d and 4s orbitals [36].

4. Conclusions

In this theoretical molecular orbital study we have considered the adsorption of c-$C_5H_5^-$ on Ni(1 1 1). This molecule bonds to the surface in a tricoordinate (hollow 3-1) site, with its five C atoms above mainly three Ni atoms. The interaction between c-$C_5H_5^-$ and Ni(1 1 1) is very strong. The electronic properties experience an extended hybridization of π orbitals and a bending away of C–H bonds. The Ni–Ni bond of the surface and the C–C bonds of the cyclopentadienyl anion are weakened after adsorption. C–Ni bonds are formed allowing the adsorption, we can see these changes in the OPs values. We find that Ni d_{z^2} orbitals and C p_z orbitals (normal to the surface) play an important role in the bonding between c-$C_5H_5^-$ and the surface. It is necessary to point out the changes after adsorption of $1e_2''$ orbital (LUMO), initially empty, is partially occupied, and the $1e_1''$ orbital (HOMO) suffers a depopulation, evidencing the adsorption process.

Acknowledgements

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