

# Characterization of the PtNi(1 1 1) surface and their influence on the selectivity of C=C and COOH bonds: A DFT study



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## ABSTRACT

The interest to study the bimetallic surfaces falls on the significant differences properties with respect to their pure components. In this work, the density functional theory (DFT) is used to study bimetallic surface compounds of a monolayer of Pt on Ni(1 1 1) and their interaction with an organic acid molecule, the cis-3-hexenoic acid. We have found significant major properties for the PtNi(1 1 1) than Ni(1 1 1) catalyst. The PtNi(1 1 1) surface is more active on the preservation of the double carbon-carbon bond of the original organic acid. The hydrogenolysis is not being promoted suggesting that the catalyst could be adequate for the industrial oils hydrogenation. The remarkable property of PtNi(1 1 1) is that it is active to the conversion from the unsaturated acid to alcohol.

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## 1. Introduction

Bimetallic surfaces present unique geometries and electronic properties for surface chemistry and catalysis [1–3]. Different kind of bimetallic systems have been searched experimentally in the past [4–8], in this work we center on a particular type of bimetallic surface: a supported metal monolayer on another metal substrate. Such a monolayer exhibits electronic properties distinct from its bulk resulting from two effects: the strain in the monolayer caused by the substrate and the mixing of the bimetallic states. The altered electronic structure can produce extraordinary surface chemistry. As an example of altered chemistry, Chen et al. [9,10] observe that cyclohexene is weakly  $\pi$  bonded on Ni/Pt(1 1 1), (di- $\sigma$ -bonded on pure Pt(1 1 1) or Ni(1 1 1)) leading to a different hydrogenation pathway [11,12]. The Ni/Pt catalysts are also of technological importance because of the presence of perpendicular magnetic anisotropy. In contrast with others systems, Ni/Pt catalysts present the perpendicular magnetic anisotropy at room temperature when the non-magnetic layers (Pt) have very small thickness (2–3 Å) [13]. Shin et al. [14] have reported the magnetic perpendicular anisotropy in Ni/Pt multilayers, as well as their magnetic properties. The local magnetism of bimetallic systems, particularly when Pt is

deposited on close packed surfaces of Ni and Co has been studied by Cabeza et al. [15].

On the other hand, in recent decades the competitive hydrogenation of carbonyl C=O and double bond C=C groups has been subject of attention [16]. The selectivity improvement is considered a difficult task, since the hydrogenation of the C=C bond on metal catalysts is usually faster than that of the C=O bond. The catalytic hydrogenation selectivity of the carbonyl group in the vicinity of the double C=C bond (isolated or conjugated) is usually carried out with VIII group metals (Pt, Rh, Ru, etc.). The performance of these catalysts in such reactions can be greatly improved by using supports of reducible oxides (TiO<sub>2</sub>, WO<sub>3</sub>, MoO<sub>3</sub>), or metal promoters (Sn, Ge, Fe) [17,18]. Generally, the improvement of the catalysts activity of transition metals supported on reducible oxides in the selective hydrogenation of the C=O bond is attributed to oxygen interaction with terminal cations of exposed oxide (for example, Ti<sup>3+</sup> in the case of titanium) or oxygen vacancies. These cations or oxygen vacancies would be created by the diffusion (spill-over) for hydrogen activation by the metal during the reduction stage [19–22]. Moreover, the best performance of promoted metal catalysts (with Sn, Ge, Fe, etc.) is attributed to the surface cations of the promoter that activate the C=O through interaction with the free electron pair of the oxygen of the carbonyl group [16,23,24]. The incidence of these effects on activity and selectivity of various types of catalysts has been studied intensively by experimental reactions such as the selective hydrogenation of alpha and beta unsaturated aldehydes. In the studies, it have been used various physicochemical characterization techniques [25–33]. The carbonyl group of the acid/fatty esters exhibits lower reactivity to the ketones and aldehydes [17].

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One of the catalysts more promising is the Sn–Ru bimetallic catalysts that are highly selective for the hydrogenation of ethyl acetate to ethanol [34], but are not selective for the hydrogenation of unsaturated fatty acids or their esters to unsaturated alcohols [35]. Costa et al. [36] found that metals promote isomerization cis-trans on unsaturated acid racing the production of alcohol.

The effects of isolated metals on the selective hydrogenation of the carbonyl in the case of VIII group metal catalysts are currently explained. However, according to our knowledge, there are no reports on the catalytic effects sets, particularly in the selective absorption of carbonyl/double C=C on bimetallic Pt–Ni surface. In this work, we use the density functional theory (DFT) to study bimetallic surface compounds of a monolayer of Pt on Ni(1 1 1) and their interaction with an organic acid molecule, the cis-3-hexenoic acid. The cis-3-hexenoic acid ( $C_5H_9COOH$ ) is an unsaturated acid that presents a double bond in the center of the chain and, due to its simple organic structure, the obtained results can be used in the prediction of the absorption and catalytic behavior of other industrial unsaturated organic acid (e.g. oleic acid). The organization of this work is as follows. In a first section we give a brief description of the theoretical method and the model employed. Afterward, a section is devoted to analyze the obtained results. We begin showing the results obtained for the absorption geometries and their implication on C=C and COOH competitive absorption. We continue presenting the electronic properties of the systems; the density of states curves was used to obtain the d-band shift of the PtNi(1 1 1) surface relative to the clean Ni(1 1 1) surface. In addition, the molecule–surface charge transfer and the PtNi(1 1 1) work function and a comparison with Ni(1 1 1) surface are presented. We end showing the results obtained for the spin polarized calculations in order to analyze the local magnetism of the PtNi(1 1 1) system.

## 2. Theory and model

We perform first-principles calculations based on density functional theory (DFT) [37,38]. The Vienna ab Initio Simulation Package (VASP) is used to solve the Kohn–Sham equations with periodic boundary conditions. We employ Blöchl's all-electron projector augmented wave (PAW) method [39,40], within the frozen core approximation. For the treatment of electron exchange and correlation, we use the PBE form of the generalized gradient approximation (GGA) [41,42]. We use a kinetic energy cutoff of 400 eV for the plane-wave basis in all calculations, which converges the total energy to 1 meV/atom. The Monkhorst–Pack scheme is used for the  $k$ -point sampling [43]. The first-order Methfessel–Paxton method [44] is used for the Fermi surface smearing.

A study shows that one Pt layer system was even more stable than the pure bulk substrate because both, the chemical affinity between the two metals in contact and, the compression in the surface plane which provides an increased electron density on the platinum sites that balance the lowered density due to the surface broken Pt bonds. On the other hand, the Pt multilayered systems were less stable than one Pt layer system because the compression destabilizes the Pt internal planes. These conclusions are compatible with experimental results [45].

We have modeled the bimetallic surface of one layer of Pt on top of four Ni(1 1 1) layers within the three-dimensionally periodic supercell (see Fig. 1). The bottom two layers of the PtNi(1 1 1) slab are kept fixed in bulk positions to represent the semi-infinite bulk crystal beneath the surface. We find that using more layers of metal substrate (and relaxing one more layer) only changes the absorption energy within the error of the calculations. In order to take into account the magnetic properties of Pt and Ni, the calculations were performed at the spin-polarized level. To model the molecule, we

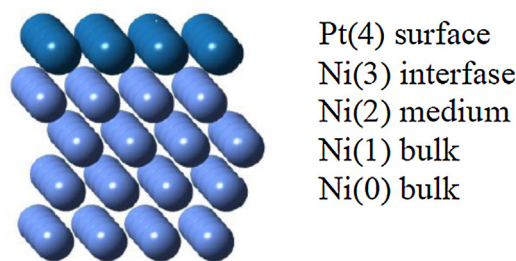


Fig. 1. Schematic view of the PtNi(1 1 1) surface showing the reference numbering for atoms according to their position in the surface model.

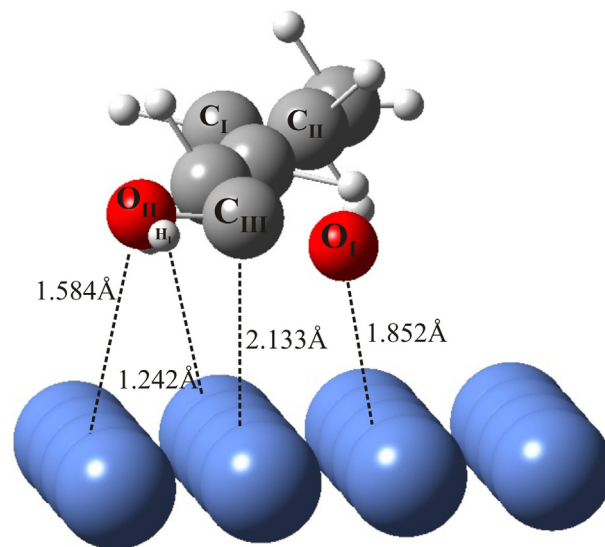


Fig. 2. Schematic view of the horizontal adsorption of cis-3-hexenoic acid on the PtNi(1 1 1) surface. For simplicity, the Pt layer is only showed.

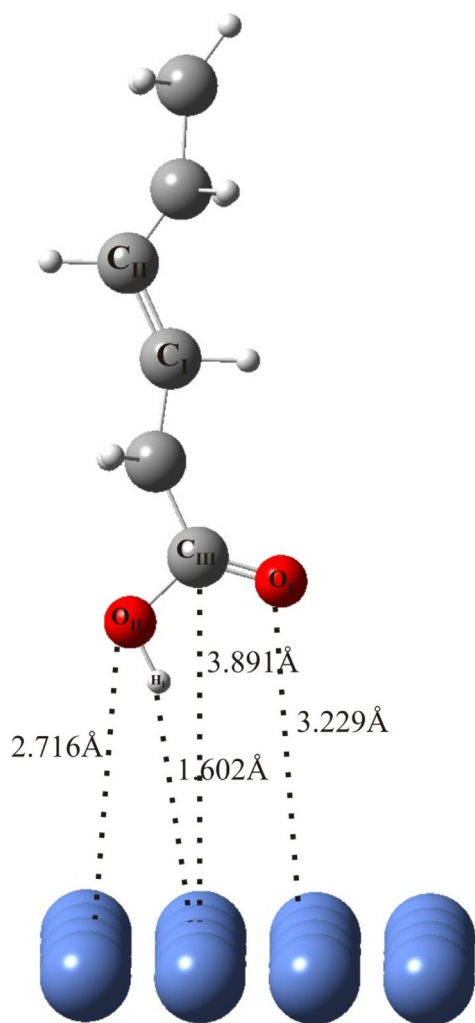
have placed it in a 20 Å cubic box. Highly symmetrical boxes can produce wrong orbital occupancies for the isolated molecule.

We explore the molecule absorption on the surface with a  $3 \times 3 \times 1$   $k$  mesh (previously checked). The molecule is allowed to relax with the top three layers of the metal substrate. When the maximum force acting on each atom of the relaxed layers drops below 0.01 eV/Å; the structural relaxation is stopped. The orbital-resolved density of states (DOS) are done with a convenient projection scheme that uses the radial cutoffs of the PAW potentials and the local magnetic moments are obtained from the difference between up-spin and down-spin local DOS integrated up to the Fermi level.

## 3. Results and discussion

The interest in analyzing the bimetallic substrates in molecule/catalyst interfaces is to show their influence in the absorption and the corresponding chemical and/or geometrical effects. On the other hand, it has generated great interest in the development of alternative catalysts that they are more active on the preservation of the double carbon–carbon bond of the original organic acid, for instance, to produce unsaturated fatty alcohols.

In order to analyze the competitive absorption between COOH and C=C chemical groups, we have considered several possible configurations that corresponds to the *vertical* and *horizontal* absorption of unsaturated  $C_5H_9COOH$  acid above the bimetallic PtNi(1 1 1) surface; after system relaxation, we have selected for the present study the most stable geometries, it can be seen in Figs. 2 and 3. When the molecule is *horizontal* adsorbed on the



**Fig. 3.** Schematic view of the vertical adsorption of cis-3-hexenoic acid on the PtNi(1 1 1) surface. For simplicity, the Pt layer is only showed.

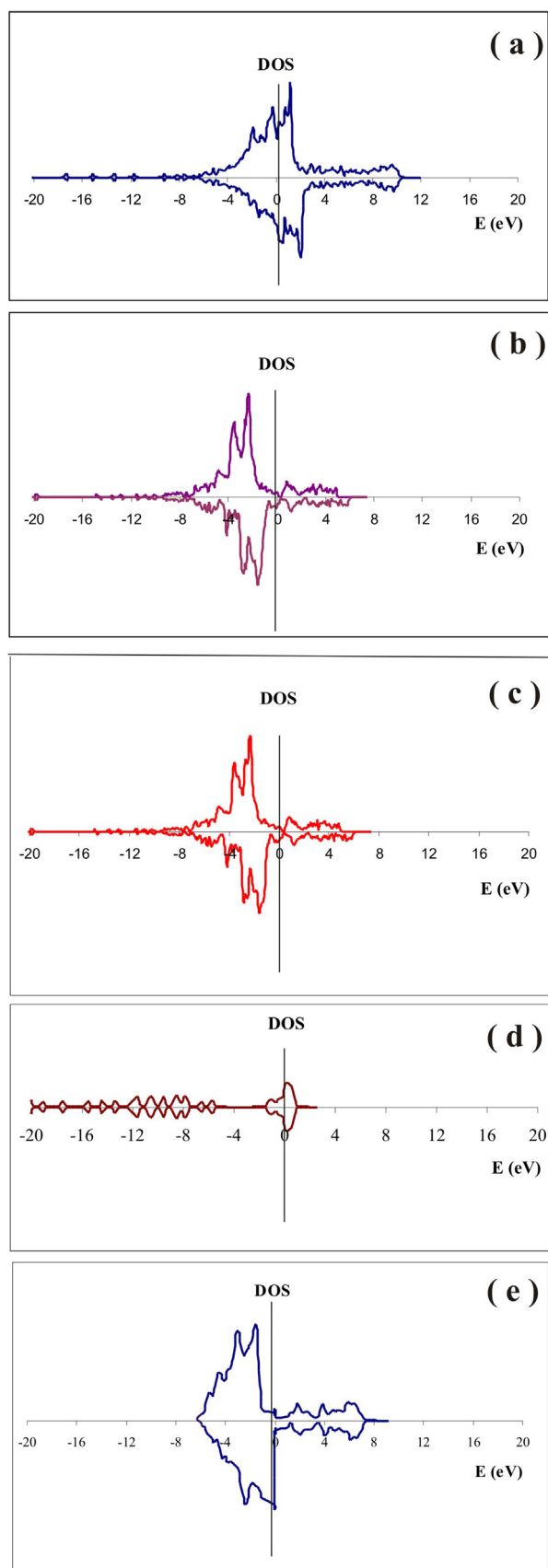
surface, their complete molecular structure has the possibility to interact with the bimetallic surface (see Fig. 2). The absorption results to be strong; we have obtained an optimum energy of  $-2.400$  eV for the relaxed system. The molecule interacts through the C=C bond but also presents interactions via the COOH group. The carboxyl group is partial dissociate: the C–OH remains tied to the molecule interacting with the surface, while the O (of C=O group) is released from the molecule and adsorbs on the surface separately; this indicates that the PtNi(1 1 1) induces the conversion from the unsaturated acid to the unsaturated alcohol. The molecule–surface optimum distances can be seen in Fig. 2. During absorption, the Pt surface atoms that interact with the molecule move away from their lattice original position and it rearranges as consequence of the strong interaction with the molecule. We can observe that the PtNi(1 1 1) surface preserves intact the double bond of the adsorbed molecule. On the other hand, the dehydrogenation of the double bond is not observed. Concerning the double bond, the absence of Pt–H interactions indicates that the hydrogenolysis is not being promoted and this condition is desired for the hydrogenation of industrial oils. We can suggest that the bimetallic PtNi(1 1 1) catalyst could be adequate for the industrial hydrogenation process. In the opposite way, when the molecule is vertical adsorbed on the surface (see Fig. 3), the interaction is weak indicative that the absorption through the carboxyl group is not favorable on the PtNi(1 1 1) surface. The molecule practically do

not present changes, their geometry remains almost the same that before adsorbed. The molecule–surface optimum distances can be seen in Fig. 3. On the other hand, we have corroborated an increased magnitude of absorption energy in comparison with the Ni(1 1 1) surface, indicating that the PtNi(1 1 1) surface does not improve the absorption of the organic acid molecule when the vertical absorption is presented or required (e.g. the production of organic films for novel electronic applications).

The bimetallic surfaces show significant differences with respect to their pure components. The d-valence levels are generally involved in this behavior and that when different metals are in contact it is possible to shift the local atomic d-bands opening a pathway to adjust the surface of transition metals in order to be more active in absorption and surface reactions. In relation, let us comment the results corresponding to PtNi(1 1 1) electronic structure. In Fig. 4(e), we present the clean Ni(1 1 1) DOS curve. We can appreciate particularly the presence to three peaks around  $-1.51$ ,  $-2.97$  and  $-4.54$  eV. Comparing, as we can see in Fig. 4(c) that three peaks also appear in the DOS of PtNi(1 1 1), they have different forms and are shifted at  $-2.25$ ,  $-3.49$  and  $-4.63$  eV. The Pt 5d-band is wider than that of pure metallic Ni(1 1 1) surface, extending up to nearly  $-7.39$  eV. In addition, the formation of Pt–Ni bonds produces depletion in the density of Pt 5d states close to  $-2.66$  eV. We have obtained the center of gravity of the d-states from the DOS curves of Ni(1 1 1) for spin polarized calculations at  $-3.45$  eV. We observe that an overlayer of Pt onto Ni(1 1 1) produces the shift of the d-band center at  $-2.51$  eV. The wider 5d-band could be justified by the difference in the energy range covered by d-band of the Pt layer that is a consequence of the reduction in the Pt–Ni distance compared with Pt–Pt distance that increases the width of the Pt d-band and the changes in the Pt–Ni(1 1 1) interactions that shift the center of the d-band to higher binding energy.

When the molecule is horizontal adsorbed on the PtNi(1 1 1) surface same states appear in the DOS and corresponds to the organic acid states (Fig. 4(a)). For comparison, Fig. 4(d) shows the states of the isolate  $C_5H_9COOH$  molecule. The system's total DOS near by the Fermi energy is dominated by the bimetallic substrate, but in a deeper energy level, the system DOS is affected by the adsorbed molecule. The hybridization effects and overlapping between the  $C_5H_9COOH$  molecule and the PtNi(1 1 1) surface have a range within  $-8$  and  $-0.5$  eV. Due the molecule–surface interaction, we can appreciate that the original three peaks observed in the clean PtNi(1 1 1) DOS curve are shifted and located at around  $1.37$ ,  $-0.22$  and  $-1.93$  eV. The new Pt-induced states now appear between  $8.25$  and  $10.67$  eV and the depletion in the density of Pt 5d states is located around  $1.14$  eV. We can also observe the states above the Fermi energy shifted in a proportional energy range. The formation of the molecule–Pt interactions increases the DOS with respect to the clean surface near the Fermi level, showing a coupling between Pt orbitals and the molecule orbitals. The magnetism of the PtNi(1 1 1) surface is observed in the unbalance between the spin-up and the spin-down states. This unbalance between the spin-up and the spin-down states decreases upon the molecule absorption. This behavior is in agreement with the decrease of the magnetic moment of interacting Pt atoms of the surface (discussed later). When the molecule is vertical adsorbed on the PtNi(1 1 1) surface (Fig. 4(b)) the obtained DOS is quite similar to the DOS of the clean PtNi(1 1 1) surface (Fig. 4(c)). The reason is the weak surface–molecule interaction and consequence, the small changes and electronic rearrangement that occur in the adsorbate and substrate atomic orbital populations.

The establishment of the bond between the molecule and the surface is reflected by the charge accumulation between the bonding species. The surface had influence on the adsorbed molecular electronic properties; consequently, we have calculated the charge transfer after absorption. For the horizontal absorption, the results



**Fig. 4.** Density of states (DOS) for (a) horizontal and (b) vertical adsorption of cis-3-hexenoic acid on PtNi(1 1 1), (c) the clean PtNi(1 1 1) surface, (d) the isolated cis-3-hexenoic acid molecule and (e) the clean Ni(1 1 1) surface.

**Table 1**

Charge for interacting surface–molecule atoms when the molecule is horizontal adsorbed on the surface.

Atom	s	p	d
C <sub>I</sub>	0.841	1.701 <sup>a</sup>	
	0.825	1.803 <sup>b</sup>	
C <sub>II</sub>	0.854	1.744 <sup>a</sup>	
	0.853	1.767 <sup>b</sup>	
C <sub>III</sub>	0.882	1.641 <sup>a</sup>	
	0.819	1.779 <sup>b</sup>	
O <sub>I</sub>	1.706	3.580 <sup>a</sup>	
	1.697	3.630 <sup>b</sup>	
O <sub>II</sub>	1.678	3.522 <sup>a</sup>	
	1.679	3.667 <sup>b</sup>	
H <sub>I</sub>	0.613 <sup>a</sup>		
	0.623 <sup>b</sup>		
Pt(4)	0.621	0.418	7.773 <sup>a</sup>
	0.685	0.567	7.812 <sup>b</sup>
	0.536	0.470	7.721 <sup>a</sup>
Pt(4)	0.685	0.567	7.812 <sup>b</sup>
	0.512	0.490	8.319 <sup>a</sup>
	0.470	0.479	8.325 <sup>b</sup>
Ni(3)	0.471	0.444	8.318 <sup>a</sup>
	0.469	0.479	8.325 <sup>b</sup>

Pt(4): atom of the surface.

Ni(3): atom of the interface.

<sup>a</sup> After the horizontal adsorption of the cis-3-hexenoic acid on the PtNi(1 1 1) surface.

<sup>b</sup> Before adsorption (isolated cis-3-hexenoic acid molecule or clean PtNi(1 1 1) surface).

show (see Table 1) that the charge transfer mainly happening on the interface between C<sub>I</sub>=C<sub>II</sub>, C<sub>III</sub>=O<sub>I</sub> and neighboring Pt atoms (see atoms reference number in Fig. 2), the major charge transfer percents are as follows: 6s Pt (−21.75%), 5p Pt (−44.09%), 5d Pt (−1.16%) and 2s C<sub>I</sub> (+1.90%), 2p C<sub>I</sub> (−5.66%) and 2s C<sub>II</sub> (−0.12%), 2p C<sub>I</sub> (−1.30%) for C<sub>I</sub>=C<sub>II</sub> bond; and 2s C<sub>III</sub> (+7.14%), 2p C<sub>III</sub> (−7.76%), 2s O<sub>I</sub> (+0.53%), 2p O<sub>I</sub> (−1.38%), 2s O<sub>II</sub> (−0.06%), 2p O<sub>II</sub> (−3.65%) and 1s H<sub>I</sub> (−1.60%) for carboxyl group. As we can see, the major changes occur in 5p, 6s Pt and 2p C, O orbitals. In general, a mixture of metallic and covalent bonding dominates across the interface, due to significant C p–Pt s,p interaction and somewhat less pronounced Pt p–Ni s,p mixing. The charge of the second nearest Ni atom modified a lesser amount, the major charge transfer percents are 5s Ni (+8.20%), 5p Ni (−7.31%) and 4d Ni (+0.12%). This indicates a majority participation of the Pt first neighbor orbitals and the influence is mainly limited to the system interface. For the vertical adsorption, the results showed in Table 2 indicate that the charge transfer mainly happens in the interface between carboxyl and neighboring Pt atoms, the major charge transfer percents are as follows (see atoms reference number in Fig. 3): 6s Pt (+5.78%), 5p Pt (−19.93%), 5d Pt (−3.71%) and 2s C<sub>I</sub> (−0.81%), 2p C<sub>I</sub> (−22.36%), 2s O<sub>II</sub> (+1.75%), 2p O<sub>II</sub> (−6.19%), 1s H<sub>I</sub> (−21.83%) for C<sub>I</sub>=O<sub>II</sub>H<sub>I</sub> bond. As we can see, the major changes occur in 4p Pt and 2p O, 1s H orbitals. The population of the second nearest Ni(3) atoms modifies a noticeable percent, especially 5p Ni orbitals: the major charge transfer percents are 5s Ni (+4.09%), 5p Ni (−45.09%) and 4d Ni (+5.59%). On the other hand, the population of the third nearest Ni(2) atoms also modifies: the major charge transfer percents are: 5s Ni (−2.06%), 5p Ni (−46.88%) and 4d Ni (+2.37%, −0.79%). As we can see, in the case of d Ni(2) orbitals, their population increase for same Ni atoms and decrease for others. These results indicate a majority participation of the Pt first neighbor and both second and third Ni neighbor orbitals in the interactions.

The work function is another parameter to evaluate adsorption. The work function change of PtNi(1 1 1) and Ni(1 1 1) surfaces result to be positive for both surfaces when adsorb the C<sub>5</sub>H<sub>9</sub>COOH molecule. The electron donation from molecule to metal is expected to decrease the work function; whereas the back-donation from the metal to adsorbate increases this property. Consequently in



**Table 2**Charge for interacting surface–molecule atoms when the molecule is *vertical* adsorbed on the surface.

Atom	s	p	d
C <sub>III</sub>	0.851	1.316 <sup>a</sup>	
	0.858	1.695 <sup>b</sup>	
O <sub>II</sub>	1.709	3.507 <sup>a</sup>	
	1.679	3.667 <sup>b</sup>	
H <sub>I</sub>	0.487 <sup>a</sup>		
	0.623 <sup>b</sup>		
Pt(4)	0.727	0.497	7.592 <sup>a</sup>
	0.685	0.567	7.812 <sup>b</sup>
Pt(4)	0.717	0.454	7.523 <sup>a</sup>
	0.685	0.567	7.812 <sup>b</sup>
Ni(3)	0.489	0.264	8.809 <sup>a</sup>
	0.469	0.479	8.325 <sup>b</sup>
Ni(3)	0.487	0.263	8.759 <sup>a</sup>
	0.470	0.479	8.325 <sup>b</sup>
Ni(2)	0.486	0.264	8.234 <sup>a</sup>
	0.499	0.497	8.300 <sup>b</sup>
Ni(2)	0.490	0.265	8.502 <sup>a</sup>
	0.499	0.497	8.300 <sup>b</sup>

Pt(4): atom of the surface.

Ni(3): atom of the interface.

Ni(2): atom of the medium.

<sup>a</sup> After the *vertical* adsorption of the *cis*-3-hexenoic acid on the PtNi(1 1 1) surface.<sup>b</sup> Before adsorption (isolated *cis*-3-hexenoic acid molecule or clean PtNi(1 1 1) surface).**Table 3**Magnetic moment for interacting surface–molecule atoms when the molecule is *horizontal* adsorbed on the surface.

Atom	Magnetic moment ( $\mu_B$ /atom)
C <sub>I</sub>	−0.004 <sup>a</sup>
C <sub>II</sub>	0.000 <sup>a</sup>
C <sub>III</sub>	−0.003 <sup>a</sup>
O <sub>I</sub>	−0.009 <sup>a</sup>
O <sub>II</sub>	0.031 <sup>a</sup>
	0.000 <sup>a</sup>
H <sub>I</sub>	0.000 <sup>a</sup>
	0.006 <sup>a</sup>
Pt(4)	0.240 <sup>b</sup>
	0.046 <sup>a</sup>
Pt(4)	0.240 <sup>b</sup>
	0.711 <sup>a</sup>
Ni(3)	0.768 <sup>b</sup>
	0.711 <sup>a</sup>
Ni(3)	0.768 <sup>b</sup>

Pt(4): atom of the surface.

Ni(3): atom of the interface.

<sup>a</sup> After the *horizontal* adsorption of the *cis*-3-hexenoic acid on the PtNi(1 1 1) surface.<sup>b</sup> Before adsorption (clean PtNi(1 1 1) surface).

our study, the bimetallic surface has positive work function change upon absorption and is characterized by a strong back-donation that over-compensates the electron donation leading to a positive dipole moment.

In order to attain a deeper description of the electronic structure of the bimetallic PtNi(1 1 1) system, it is shown in Tables 3 and 4 the calculated local magnetic moments for the different atoms of our model. The atom number indicates the position of the metallic atoms in the slab: Ni(1) (bulk), Ni(2) (medium), Ni(3) (interface) and Pt(4) (surface) (see Fig. 1). It is a well-known property that the magnetic moment of Pt and Ni atom differs, according our calculations the obtained values are 0.24 and 0.77, respectively, in the clean PtNi(1 1 1) surface. After the *horizontal* absorption of the C<sub>5</sub>H<sub>9</sub>COOH molecule, the bimetallic surface present the major magnetic moment changes in Pt atoms (see Table 3). The magnetic moment decreases from 0.24 to 0.006 for Pt(4) atoms interacting with the C<sub>I</sub>=C<sub>II</sub> bond, while a decrease from 0.24 to 0.046 is produced for Pt(4) atoms that interact with the C<sub>III</sub>=O<sub>I</sub> bond. These

**Table 4**Magnetic moment for interacting surface–molecule atoms when the molecule is *vertical* adsorbed on the surface.

Atom	Magnetic moment ( $\mu_B$ /atom)
C <sub>III</sub>	−0.026 <sup>a</sup>
O <sub>II</sub>	−0.114 <sup>a</sup>
H <sub>I</sub>	−0.002 <sup>a</sup>
Pt(4)	0.017 <sup>a</sup>
	0.240 <sup>b</sup>
Pt(4)	0.027 <sup>a</sup>
	0.240 <sup>b</sup>
Ni(3)	0.321 <sup>a</sup>
	0.768 <sup>b</sup>
Ni(3)	0.359 <sup>a</sup>
	0.768 <sup>b</sup>
Ni(2)	0.812 <sup>a</sup>
	0.706 <sup>b</sup>
Ni(2)	0.575 <sup>a</sup>
	0.706 <sup>b</sup>

Pt(4): atom of the surface.

Ni(3): atom of the interface.

Ni(2): atom of the medium.

<sup>a</sup> After the *vertical* adsorption of the *cis*-3-hexenoic acid on the PtNi(1 1 1) surface.<sup>b</sup> Before adsorption (clean PtNi(1 1 1) surface).

changes are due to the presence of the new interactions formed between the molecule and the surface. As we can see, the major magnetic moment change is produced when the double bond interacts with the surface corroborating that the double C=C interacts stronger than the COOH group highlighting the C=C selectivity. The magnetic moment of Ni(3) also changes after absorption but in a very lesser percent (see Table 3). The results show that the magnetic moments were mainly induced on the molecule atoms by the surface proximity (see Table 3). The magnetic moment is much larger for those atoms closer to the Pt layer where the proximity effect is clearly stronger. As we can see in Table 3, a magnetic moment is induced in the molecule atoms that participate in the interactions. The reason is the C 2p and O 2p population and density of states was changed after absorption inducing a charge transfer and hybridization interaction. When the C<sub>5</sub>H<sub>9</sub>COOH molecule is *vertical* adsorbed on the PtNi(1 1 1) surface, the bimetallic surface also present the major magnetic moment changes in Pt atoms (see Table 4). The magnetic moment decreases from 0.240 to 0.017 for Pt(4) atoms interacting with the C<sub>I</sub>=O<sub>II</sub> bond. The changes are smaller than in the *horizontal* absorption because the molecule interacts weaker with the surface. The magnetic moment of Ni atoms also change after absorption from 0.706 to 0.321 and 0.768 to 0.575 in the case of second Ni(3) and third Ni(2) neighbors, respectively (see Table 4). Important magnetic moments were induced on the molecule atoms by surface proximity (see Table 4). As we can see in Table 4, negative magnetic moment values are obtained for the C<sub>I</sub>, O<sub>II</sub> and H<sub>I</sub> atoms due their participation in the interactions with the PtNi(1 1 1) surface.

#### 4. Conclusions

The bimetallic PtNi(1 1 1) surface present notable properties with respect to the pure component and they can be resuming as follows:

- The PtNi(1 1 1) catalyst is more active on the preservation of the double carbon–carbon bond of the original organic acid than the Ni(1 1 1) catalyst.
- The hydrogenolysis of the double bond is not being promoted. We propose that the bimetallic PtNi(1 1 1) catalyst could be adequate for the industrial oils hydrogenation.
- We suggest that the bimetallic PtNi(1 1 1) surface is not adequate for the use as organic films.

- The remarkable property of PtNi(1 1 1) is that it is active to the conversion from the unsaturated acid to unsaturated alcohol.

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