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Platinum-nickel catalyst: The effect of promoters in *cis*-oleic acid adsorption

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ABSTRACT

The study of the *cis*-oleic acid adsorption, on clean and promoted (K, Mg, Co, B or Pd) PtNi(1 1 1) surface was performed by quatum chemical calculations. The oleic acid adsorption on PtNi(1 1 1) surface shows a weak molecule–surface interaction. No preferential site for C=C adsorption is computed and only the C=O adsorption is favored on the clean PtNi(1 1 1) surface. The adsorption properties of the PtNi(1 1 1) are improved by promoters. The stability of the system is increased and the C=C/surface distances are reduced when promoters are present. Among the considered promoters, Co has the best performance in terms of system stability. The lowest C p orbital substantially interacts with Pt and Co s, p and d orbitals. The change electron density of metal centers, enhance the C=C adsorption being the Pt–C interaction the more favored. After adsorption, the strength of the C=C, Pt—Pt and Pt—Co bonds decrease while a molecule–surface bond is formed.

1. Introduction

The increase in the saturation degree of fatty acids by hydrogenation has been made on a large scale since the beginning of last century. In parallel with double bond saturation, other reactions such as double bond migration and *cis*/*trans* isomerization take place during the hydrogenation. The industrial process is actually carried out in gas–liquid (hydrogen-oil) phases, which are in contact with a Ni catalyst in a semi batch reactor at 180 °C and 5 bar. Recent studies on "good" and "bad" fats have added a new dimension to the practical and technical aspects of oil hydrogenation. *Trans*-isomers are thermodynamically favored during the hydrogenation and the significance of *trans*-fatty acids to human health was subject of debate for decades. Several studies showed that *trans*-fatty acids may affect plasma lipoproteins levels – lowering the concentrations of high-density lipoprotein (HDL) cholesterol (good cholesterol) and increasing the concentrations of low-density lipoproteins (LDL) cholesterol (bad cholesterol) [1,2]. A relationship between the high ingestion of *trans*-fatty acids and an increase in the risks of coronary diseases has also been established [3]. From these considerations arises the need to search for alternatives that improve the catalytic process in order to reduce the *trans*-isomers content in hydrogenated edible oils. A field where much progress has been made is the design of new hydrogenation catalysts. Supports with specific properties and a sharply defined pore structure have been studied; several active metals have been used (Pt, Pd, Rh, In) obtaining differences in the *cis*/*trans* and saturate compounds selectivity [4]. Active metals, i.e., palladium, copper, ruthenium, cobalt, platinum, have been researched, especially for the purpose of reducing *trans*-fatty acids contents. The performance parameters, e.g., activity and selectivities, vary significantly with the catalyst types and reaction conditions [5]. A theoretical study was also carried out using molecular mechanics and the extended Hückel method (EHMO) to analyze the hydrogenation and *cis*/*trans* isomerization mechanisms of the oleic acid [6] and a new research direction can be established in the search for a reduction of the *trans* fatty acid content in partially hydrogenated oils.

The use of alkali metals as promoters on alumina and silica-supported palladium catalyst was studied several years ago [7,8]. Pd and Pd–Me (Me = Mo, V and Pb) supported catalysts were studied for the sunflower oil hydrogenation [9,10]. Anodized aluminum monolithic catalysts impregnated with palladium have been investigated in the sunflower oil hydrogenation reaction [11]. This monolithic catalysts showed a 50% C=C conversion in 30 min. A loss of activity was observed, decreasing 80% in the sixth test, which was related to the presence of carbonaceous residues in the catalyst surface [11]. The partial hydrogenation of sunflower oil with minimum *trans*-isomer formation was studied, using a Pd/γ-alumina catalyst modified with promoters allowed for human diet: ethyl benzoate and magnesium glycinate. Regarding the *cis*/*trans*-selectivity, significant differences were found: ethyl benzoate increases the formation of *trans*-isomers, whereas magnesium glycinate

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decreases it. These results can be interpreted in terms of different effects: change in the electron density of palladium, which affects the relative adsorption strength of the reactant, intermediates and hydrogen; and a block of part of the surface, by the promoters. Theoretical calculations of sunflower oil hydrogenation were conducted to support this hypothesis [12]. In this study, the catalyst was modified: (a) with K and (b) by high temperature reduction treatment, in order to observe its influence on the activity and the *cis*-isomers selectivity. Regarding selectivity, the formation of *trans*-isomers was higher in the reaction under conventional conditions, whereas the production of saturated compound was favored in the homogeneous operation. Pt-K/TiO_2 and Pt/TiO_2 catalyst presented a similar TON (turnover number), although the *cis*-isomer selectivity increased with the alkali addition [13]. Additives containing nitrogen compounds in liquid phases were also tested, finding a better (yet small) *cis*-selectivity attributed to the modification of the chemisorption ability of the active metals centers [14]. Soybean oil was hydrogenated by amorphous Ni–B alloy nanocatalysts reducing the formation of both *trans*- and saturated fatty acids in hydrogenated products. The Ni-B catalyst had a lower selectivity towards formation of *trans*-fatty acids but a higher selectivity towards formation of stearic acid than the commercial nickel catalyst. The incorporation of boron to nickel-containing catalysts increased the selectivity ratio but did not change the linolenic selectivity [15].

In a recent work, our group studied the *cis*-oleic acid adsorption on Ni(1 1 1) surface by theoretical calculations [16]. *Cis*-oleic acid is a monounsaturated omega-9 fatty acid used in food industry, pharmaceutics, medicine, and novel electronic applications, such as optoelectronic devices, sensors, field effect transistors, and dielectrics [17,18]. The theoretical study was performed using the Atom Superposition and Electron Delocalization Molecular Orbital (ASED-MO) calculations [16]. Competitive adsorption analysis of C=C vs. C=O bonds proved that parallel to the surface C=C adsorption dominates the adsorption process. The electronic and bonding properties of the molecule in the region close to the double bond are modified, while the adsorption energy depends on the adsorption site coordination geometry. The adsorption with the center of the double carbon bond placed above a three-fold octahedral position was identified to be the most favorable in terms of energy. Ni—Ni, C=C, and C—C bonds are weakened upon adsorption while new bonds between carbons from the double bond and the nickel surface are formed. The main bonding interactions are Ni 4p and Ni 3d with the C 2p orbitals. In addition a weak Ni—H bonding interaction is also detected [16].

From the point of view of activity, platinum is more efficient catalyst than nickel [19] and, on the other hand, platinum was reported as one of the catalysts with better *cis*-isomers selectivity [20]. The objective of the present work is to study by theoretical calculations the adsorption of *cis*-oleic acid, first, on a PtNi(1 1 1) surface, and then on the same surface modified with different promoters: K, Mg, Co, B or Pd atoms. The theoretical method and the adsorption model are described in the next section.

2. Theoretical method and adsorption model

The calculations were performed using the ASED-MO method which is a modification of the classical EH-MO method [21]. The PtNi(1 1 1) surface was modeled using a two dimensional slab of finite thickness, so as to better simulate the metallic surface. A five-layer slab was employed as a compromise between computational economy and reasonable accuracy. The slab have the following design: the top is a Pt(1 1 1) layer and the rest (four layers) are Ni(1 1 1) layers. Only the first three layers of the slab and the oleic acid molecule were allowed to relax. The molecule was adsorbed on the Pt(1 1 1) layer. We adopted the initial molecular structure of the *cis*-oleic acid reported by Misra et al. [22]. During calculations, the structures of both molecule and substrate were optimized at steps of 0.02 Å and at an energy convergence of 0.01 eV. Four sites were examined for the oleic acid parallel to the surface adsorption on PtNi(1 1 1) (that means, C=C parallel to the surface), designated in order of increasing coordination number: on top (1C), bridge (2C), hcp (3CO), and fcc (3CT), (see Fig. 1). The *cis*-oleic acid molecule has also the possibility to be adsorbed on the surface through the carboxylic group (—COOH) (see Fig. 1). In order to check this competitive adsorption of —COOH and C=C chemical groups, we considered the “vertical” adsorption of the oleic acid on the same 1C, 2C, 3CT and 3CO sites.

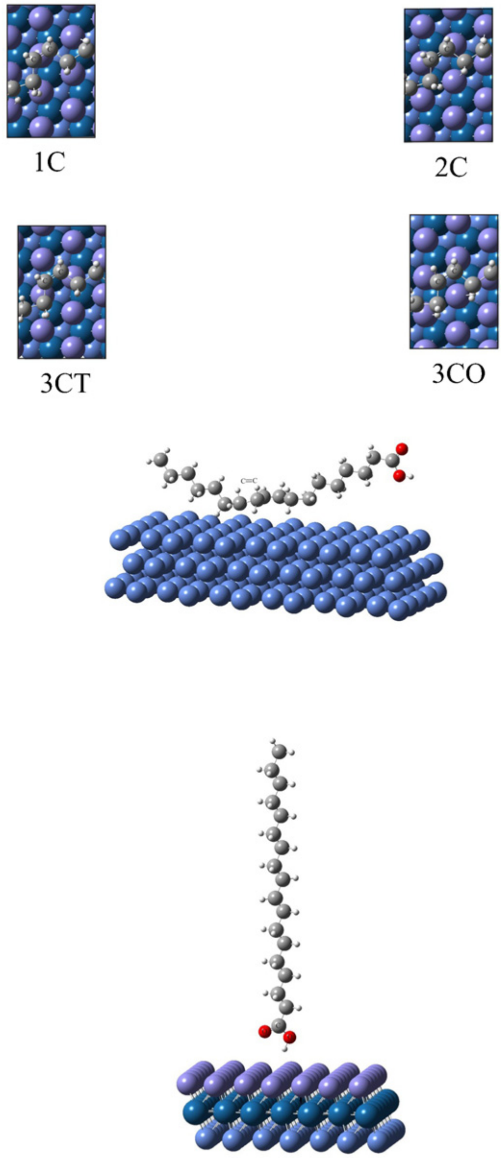

Fig. 1. Schematic top view of the C=C adsorption sites on the PtNi(1 1 1). Lateral views of the parallel and vertical *cis*-oleic acid adsorption on PtNi(1 1 1) surface.

The adiabatic adsorption energy (E_{ads}) values were calculated by:

$$E_{ads} = E_T(OA/PtNi(1\,1\,1)) - E_T(OA) - E_T(PtNi(1\,1\,1)) \qquad (1)$$

where OA/PtNi(1 1 1), OA, and PtNi(1 1 1) refer to the *cis*-oleic acid molecule-on-platinum/nickel slab system, the free *cis*-oleic acid molecule, and the isolated platinum/nickel slab, respectively.

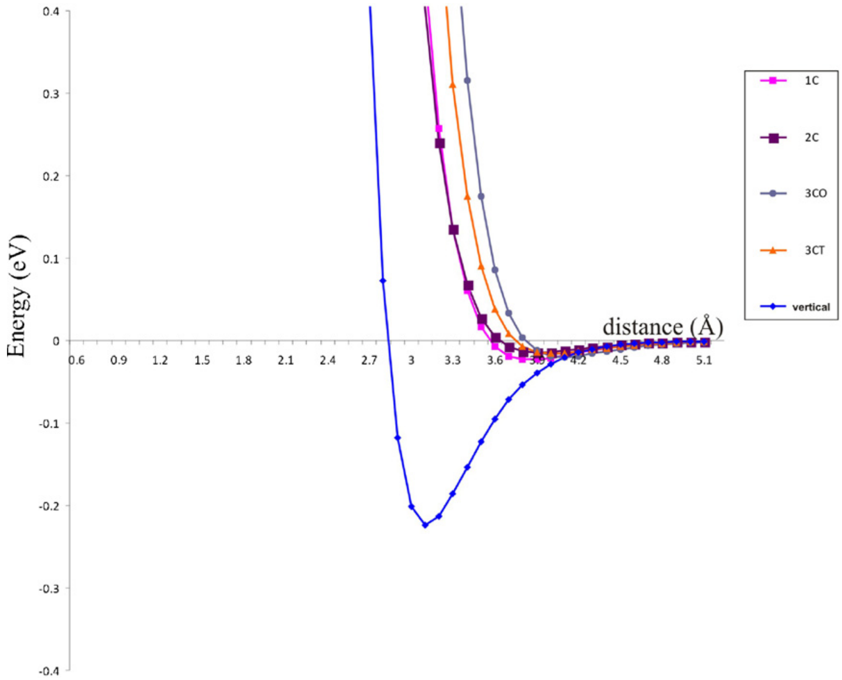

Fig. 2. Adiabatic energy curves for the different adsorption sites of *cis*-oleic acid adsorption on PtNi(1 1 1) surface.

The molecule–surface distance was optimized in order to get the total energy minima and to determine the preferential adsorption site.

In a second part, we modified the PtNi(1 1 1) surface adding promoters (Pr), (Pr = K, Mg, Co, B or Pd atoms). In this case, the adiabatic energy (E_{ads}) values were calculated by:

$$E_{ads} = E_T(\mathrm{OA/PrPtNi(1\ 1\ 1)}) - E_T(\mathrm{OA}) - E_T(\mathrm{PrPtNi(1\,1\,1)}) \tag{2}$$

where OA/PrPtNi(1 1 1), OA, and PrPtNi(1 1 1) refer to the *cis*-oleic acid molecule-on-promoter/platinun/nickel slab system, the free *cis*-oleic acid molecule, and the isolated promoter/platinum/nickel slab, respectively.

The electronic structure and chemical bonding were also analyzed. We used the yet another extended Hückel molecular orbital package (YAeHMOP) for the construction of the density of states (DOS) curves and the crystal orbital overlap population (COOP) curves [23]. This method properly captures essential orbital interactions in chemisorption [24] and was successfully used in our previous study [16].

3. Results and discussion

Let start considering the parallel adsorption of *cis*-oleic acid on the PtNi(1 1 1) surface. The energy/distance curves corresponding to the examined four sites (1C, 2C, 3CT and 3CO) are shown in

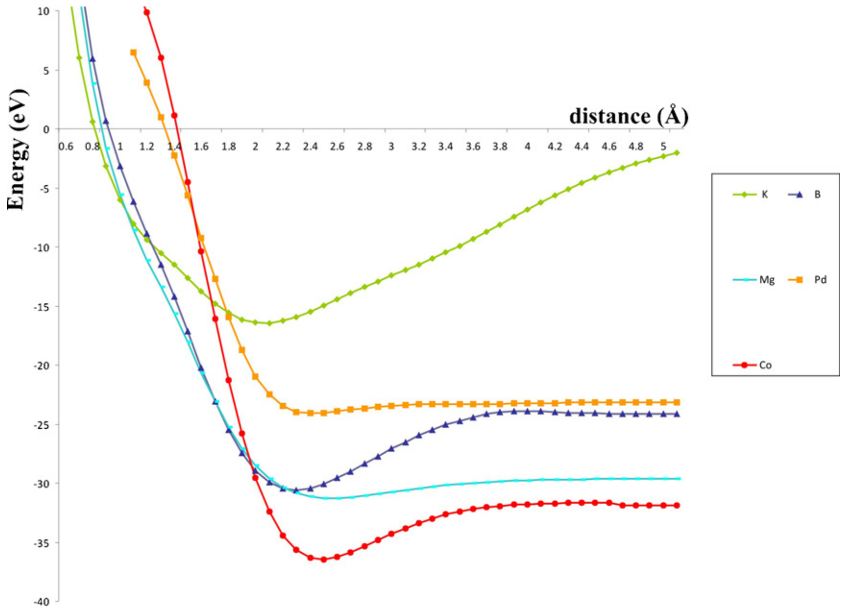

Fig. 3. Adiabatic energy curves for *cis*-oleic acid adsorption on PtNi(1 1 1) surface modified with K, Mg, Co, B or Pd promoters.

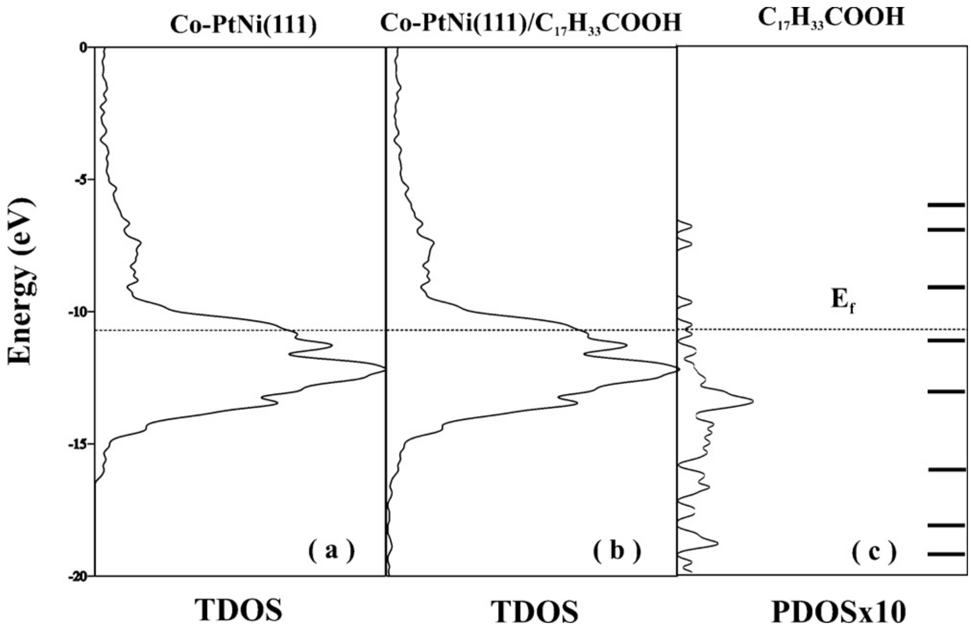

Fig. 4. (a)Total DOS for the Co-PtNi(1 1 1) isolated system, (b) total DOS for the Co-PtNi(1 1 1)/$C_{17}H_{33}COOH$ system and (c) projected DOS for the $C_{17}H_{33}COOH$ molecule adsorbed on the surface. The horizontal solid lines indicate the orbital positions in the isolated $C_{17}H_{33}COOH$ molecule.

Fig. 2. It can be seen that the energy curves for the molecular horizontal adsorption are similar and do not present a well-defined minima indicating a weak molecule–surface bonding. There is not preferential site for C=C adsorption on the PtNi(1 1 1) surface and the double bond is located far away from the surface, at distances between 3.8 and 4.1 Å. However, the vertical oleic acid adsorption geometry on the PtNi(1 1 1) surface is favored (see blue line in Fig. 2). The —COOH group is located at 3.1 Å to the surface, at the minimum energy position site (3CO). Analyzing the competitive adsorption between C=O and C=C chemical groups, the PtNi(1 1 1) surface is more stable when the *cis*-oleic acid molecule interacts through the C=O group. This is an important property because the hydrogenation of the C=C bond on metallic catalysts is normally much faster than that of the C=O bond [25] and this is critical for the selective hydrogenation of the oleic acid and/or of its esters to the unsaturated alcohols. The adsorption of *cis*-oleic acid on the PtNi(1 1 1) surface is less favorable than on the Ni(1 1 1) surface [16]. In other words, the addition of platinum layer on the top of the Ni(1 1 1) surface does not show a noticeable improvement in adsorption.

Different promoters: K, Mg, Co, B or Pd atoms were pre-adsorbed on the PtNi(1 1 1) surface. As mentioned before, in absence of a preferential adsorption site, we selected a 3CO site to study the oleic acid horizontal adsorption on the modified surfaces. Fig. 3 shows the energy curves for the different systems. It can be seen that all the systems are more stable than the clean surface. The curves corresponding to Pd and Mg promoters do not present an unique minima position for oleic acid molecule. The curves corresponding to K, Co and B promoters present well-defined minima, showing a strong molecule–surface interaction. In general, the C=C/surface distances are between 2.1 and 2.6 Å which are shorter than those on the PtNi(1 1 1) surface without promoters. We can conclude that promoter atoms improve the molecule–surface contact giving place to better adsorption energies.

The Co promoter curve present the best energy minimum with the C=C adsorbed at 2.6 Å to the surface; then, in order to analyze the molecule–surface interactions, we have study in detail the electronic structure and bonding characteristics of this system. It can be seen in Fig. 4(a) the DOS curve corresponding to the isolated PtNi(1 1 1)–Co system. When the molecule is adsorbed, the changes are mainly located at low energy values (see Fig. 4(b)). For a better view of these states, the partial DOS of the free *cis*-oleic acid, arranged in the same geometry as adsorbed, is shown in Fig. 4(c). All molecular orbitals are located at lower energy values compared to the isolated species, representing an energetic stabilization of the molecule after adsorption. The lowest p orbital of the molecule substantially interacts with metal orbitals and the corresponding bands are spread out after adsorption.

The orbital populations and net charge are modified after molecule–surface interaction (see Table I and references in Fig. 5). The substrate–adsorbate interaction mainly comes from the contact between C=C and their neighboring C—C, C—H bonds, and Co and Pt atoms from the surface. Due to the molecular symmetry, we have only reported the atoms and their interactions at one side of the double bond (the interactions are similar on the other side). The C 2p orbital population decreases to about 13%. The changes came from p_x(10–25%), p_y(8–9%) and p_z(8–19%) orbitals. The C 2s orbital only change 0.6–1.2%. The H 1s orbital population (H—C=C bond) diminishes 0.2% (each C atom of the double bond lies on a Pt atom respectively. The Pt electron orbital population change after adsorption). The Pt 4s, Pt 4p and Pt 3d decrease to about 5%, 3% and 2% respectively. The mainly changes are denoted in d_{z^2}

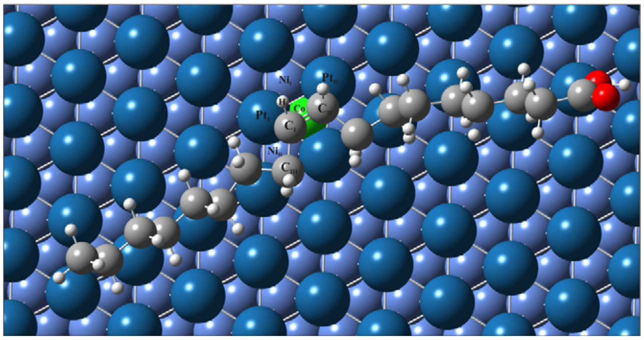

Fig. 5. Schematic top view of the oleic acid adsorption on Co-PtNi(1 1 1) surface Pt ● Ni ● Co ● C ● H ○ O .●

Table I
Electron orbital occupations and net charges for selected atoms.

Atom	s	p_x	p_y	p_z	$d_{x^2-y^2}$	d_{z^2}	d_{xy}	d_{xz}	d_{yz}	Charge
C_I	0.9900	0.8020	1.0297	0.8800	–	–	–	–		0.298[a]
	1.0005	0.9721	1.1402	1.0296						−0.142[b]
C_{II}	0.9882	0.9489	0.8666	0.8701						0.326[a]
	0.9944	1.2676	0.8672	0.9489						−0.078b
C_{III}	0.9652	0.8504	0.8335	0.8465						0.504[a]
	0.9536	0.9416	0.9104	1.0510						0.867[b]
H_I	0.9468									0.053[a]
	0.9483									0.052[b]
Pt_I	0.7800	0.4580	0.4294	0.4075	1.1927	1.3093	1.2330	1.2982	1.3323	1.560[a]
	0.8216	0.4722	0.4459	0.4211	1.1837	1.5352	1.2171	1.2297	1.3274	1.346[b]
Co	0.2446	0.0205	0.0233	0.0052	0.4923	0.2641	0.4758	0.7415	0.7441	6.087[a]
	0.2836	0.0225	0.0229	0.0469	0.4749	0.3774	0.4727	0.7621	0.7673	5.860[b]

[a] $C_{17}H_{33}COOH$/Co–PtNi(1 1 1) system.
[b] Isolated $C_{17}H_{33}COOH$ or bare Co-PtNi(1 1 1) surface.

(14%), d_{xz} (6%), s (5%) and p_y (4%) orbitals. The promoter's orbital population also changes after adsorption. The Co 4s, 4p and 3d population decreases 14%, 47% and 5% respectively. The Co major changes involves the p_z (89%), $d_z{}^2$ (30%), s (14%) and p_x (9%) orbitals. The change in the electron density of Pt and Co affects positively the adsorption strength of the C=C bond. This means that electrons are exchanged in the valence band making the surface bonds with the molecule's orbitals. A bonding between C and Pt arises because of the closeness of C 2p valence levels to s–d states from Pt bands. The corresponding changes in the overlap population (OP) are presented in Table II The COOP curve shows an important C—Pt bonding interaction (see Fig. 6(a) in the −11 eV to −18 eV region). The adsorption of the olefinic bond is strengthened comparing with *cis*-oleic acid adsorption on the Ni(1 1 1) surface (0.293 vs. 0.047 [16]). In addition, a small H—Co bonding interaction is detected (see Table II and Fig. 6(b)). This H–surface interaction on the Co–PtNi(1 1 1) system is smaller than the H–Ni(1 1 1) interaction (surface without Pt and Co). The smaller H–Co interaction could indicate that the H—C bond weakening is not promoted. The described bonding picture is desired for the oils hydrogenation in industrial process.

The bonding is also analyzed considering the strength changes of C=C, C—C, C—H bonds and the Pt—Pt, Pt—Ni, Ni—Ni, Pt—Co bonds, comparing the OP bonds before and after adsorption (see Table II).

Table II
Overlap population (OP) for selected atoms.

Bond	OP	
	Before[b]	After[a]
C_I=C_{II}	1.170	0.913
C_I—C_{III}	0.834	0.817
C_I—H_I	0.867	0.856
Pt_I—Pt_{II}	0.406	0.355
Pt_I—Ni_I	0.196	0.200
Ni_{II}—Ni_{III}[c,d]	0.155	0.160
Pt_I—Co	0.723	0.652
C_I—Pt_I		0.293
H_I—Co		0.001

[a] $C_{17}H_{33}COOH$/Co–PtNi(1 1 1) system.
[b] Isolated C17H33COOH or bare Co–PtNi(1 1 1) surface
[c] Ni_{II}, is Ni_I nearest neighbor, corresponding to the second close-packed FCC (1 1 1) plane.
[d] Ni_{III} is Ni_{II} nearest neighbor, corresponding to the third close-packed FCC (1 1 1) plane, located below Co atom.

The C=C, C—C, C—H bond strength decrease 22%, 2% and 1% respectively; while the Pt—Pt, Pt—Ni, Ni—Ni and Pt—Co bond strength decrease 13%, 2%, 3% and 10% respectively, after adsorption. Then, the major changes developed in the C=C, Pt—Pt and Pt—Co bonds as shown in Table II If we compare COOP curves in Fig. 7, a smaller OP is observed after adsorption indicating a weakening of C=C, Pt—Pt and Pt—Co bonds while a Pt—C bond is developed. It can be seen, the C=C and Pt—Co OP curves show an increased unoccupied antibonding states after adsorption, while Pt—Pt OP curve shows a decreased bonding states after adsorption (see Fig. 7). Similar methodology is presented by Shuttleworth when described adsorbate–metal surface bonding [26]. To better understand the nature of these changes, we compared the orbital by orbital contributions to Pt—Pt, Pt—Co and C=C overlap populations (OP) before and after adsorption, the more important results are showed in Table III. The major Pt–Pt OP changes can be seen in Pt p_z–Pt p_z (−99%), Pt d_{yz}–Pt d_{yz} (+93%), Pt p_y–Pt $d_z{}^2$ (+85%), Pt p_z–Pt d_{yz} (−79%) and Pt s–Pt $d_z{}^2$ (+53%) orbitals; while the major Pt–Co OP changes occur in Pt $d_z{}^2$–Co $d_z{}^2$ (−52%), Pt $d_x{}^2{}_y{}^2$– Co $d_z{}^2$ (−49%), Pt d_{xz}–Co $d_z{}^2$ (−46%), Pt s–Co s (−26%) and Pt p_z–Co d_{yz} (−13%) orbitals. The C=C OP changes can be detected

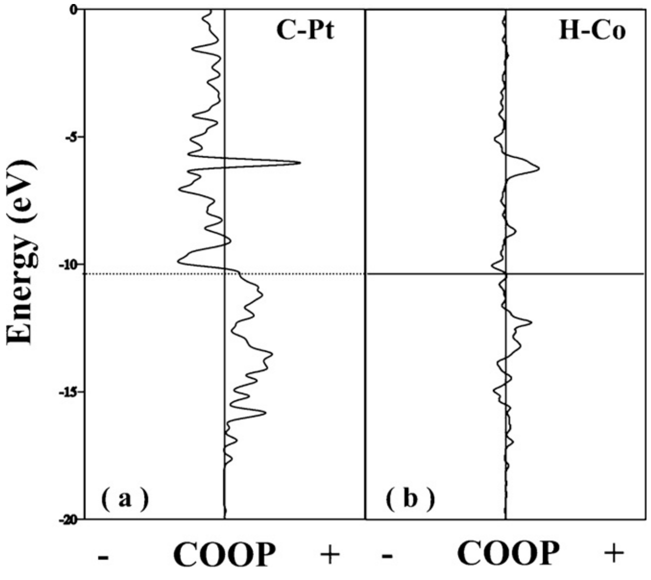

Fig. 6. COOP curves for the (a) C–Pt and (b) H–Co interactions after adsorption.

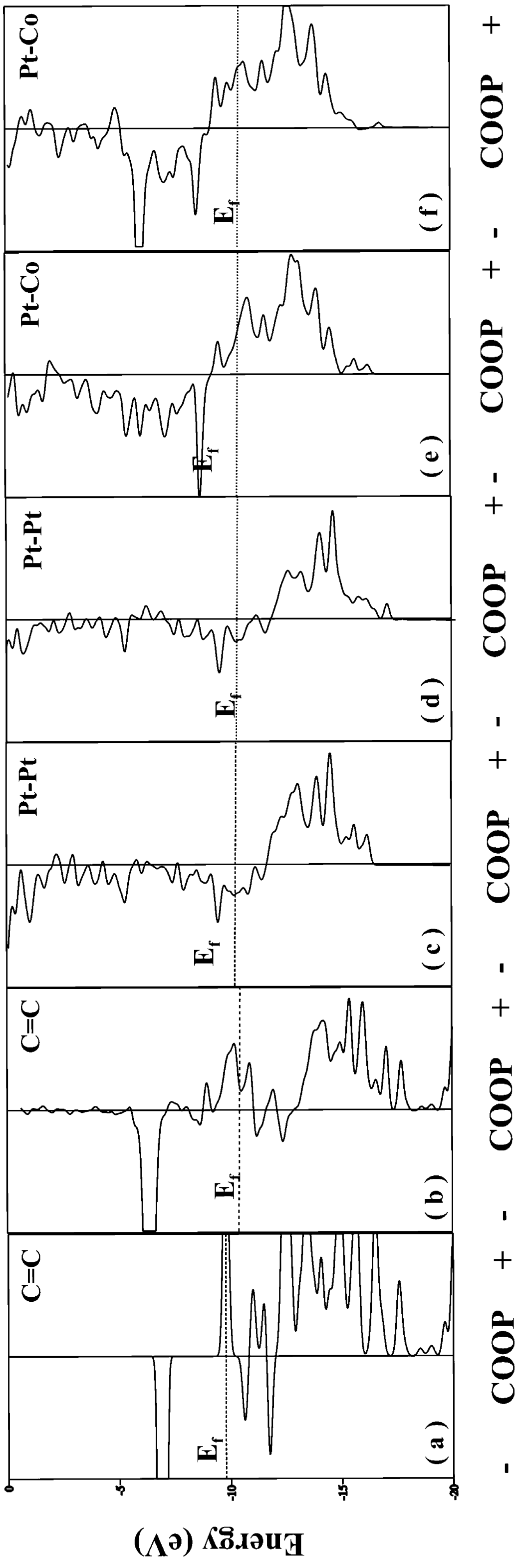

Fig. 7. COOP curves for the C=C, C—C and C—H bonds (a), (c), (e) before and (b), (d), (f) after adsorption.

in C p_z–C p_z (−57%), C p_x–C p_x (−47%), C p_x–C p_y (−47%), C s–C p_x (+41%) and C s–C p_y (+23%) orbitals. These changes affect positively the adsorption strength of the C=C bond making possible the molecule–surface bonding.

Table III
Major orbital by orbital changes to Pt—Pt, Pt—Co and C=C overlap populations (OP).

	Pt—Pt	
	Before[b]	After[a]
s–d_{z^2}	0.0056	0.0087
p_y–d_{z^2}	0.0070	0.0130
p_z–p_z	0.0014	0.0001
p_z–d_{yz}	0.0015	0.0033
d_{yz}–d_{yz}	0.0056	0.0109

	Pt—Co	
	Before[b]	After[a]
s–s	0.0781	0.0578
p_z–d_{yz}	0.0318	0.0275
$d_{x^2y^2}$–d_{z^2}	0.0004	0.0002
d_{z^2}–d_{z^2}	0.0589	0.0284
d_{xy}–d_{z^2}	0.0011	0.0006

	C=C	
	Before[b]	After[a]
s–p_x	0.1105	0.1563
s–p_y	0.0776	0.0957
p_x–p_x	0.1112	0.0589
p_x–p_y	0.1476	0.0782
p_z–p_z	0.3694	0.1582

[a] $C_{17}H_{33}COOH$/Co–PtNi(1 1 1) system.
[b] isolated $C_{17}H_{33}COOH$ or bare Co–PtNi(1 1 1) surface.

4. Conclusions

The computational study of the *cis*-oleic acid adsorbed, first, on a PtNi(1 1 1) surface, and then, on promoter-PtNi(1 1 1) modified surfaces (promoter = K, Mg, Co, B or Pd atoms) were performed by ASED-MO calculations. The *cis*-oleic acid adsorption on PtNi(1 1 1) surface shows a weak molecule–surface interaction and the C=C bond is located far away from the surface. No preferential site for C=C adsorption is detected and only the C=O adsorption is favored on the PtNi(1 1 1) surface. The adsorption properties of the PtNi(1 1 1) are then improved when promoters are added. The exposed metallic surface is then modified changing the adsorption strength of the reactant. The stability of the system increase and the C=C/surface distances are reduced when the adsorption is performed by promoters. Co promoter shows the best adsorption properties. From the electronic structure and bonding analysis, all molecular orbitals of *cis*-oleic acid are located at lower energy values compared to the isolated specie representing an energetic stabilization of the molecule after adsorption. The lowest C 2p orbital substantially interacts with Pt and Co s–d orbitals. The main overlap population corresponds to the C–Pt interaction. After adsorption, the strength of C=C, Pt—Pt and Pt—Co bond changes favoring the molecule–surface interaction.

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