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Computational study of *cis*-oleic acid adsorption on Ni(1 1 1) surface

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ABSTRACT

In the present work, the Atom Superposition and Electron Delocalization method has been applied in order to study the adsorption of *cis*-oleic acid on Ni(1 1 1) surface. This molecule presents two active functional groups, C=C (in the middle) and –COOH (at one end). Therefore, it is important to explore adsorption on the metal surface through the C=C bond in a geometry parallel to the surface and also in a vertical one with –COOH pointing at Ni atoms. Our results indicate that the parallel geometry is more stable than the vertical one and C=C bond adsorption dominates the process. Energetic results show a strong interaction with the metallic surface. Ni–Ni, C=C, and C–C bonds are weakened upon adsorption because of a bonding interaction between carbons and nickel surface. We found that Ni 5d_z² and 5d_{yz} orbitals play an important role in the bonding between C p_x, p_z orbitals and surface, and the same happens with Ni 6p_x and Ni 6p_z. A small Ni–H interaction is also detected.

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1. Introduction

Simultaneous reactions occur during hydrogenation of edible fats containing carbon–carbon bonds: double bonds can be saturated, migrated or isomerized from *cis* to *trans*. The aim, in fat hydrogenation, is to avoid the formation of *trans* and totally saturated products. In fact, the effects on human health of *trans* fats have received increasing attention [1,2] and they are considered to be as detrimental as saturated fats [3]. Some results indicate that *trans* fatty acids can favor cardio-vascular diseases [4,5]. Dietary studies have shown the potentially harmful effects of *trans* acids on human LDL/HDL-cholesterol ratio [6,7]. *Trans* isomers usually appear in oil subject to thermal treatment at 190 °C. For this reason, there were various attempts to reduce *trans* fatty acid content in food products, especially in hydrogenated edible fats [8–10]. Jacobs [11] showed that the formation of harmful *trans* unsaturated fatty acids can be avoided using zeolites due to “their shape selectivity” property. The carbonyl group of the unsaturated fatty ester is specifically adsorbed over the active sites located at the pore opening of zeolites in order to inhibit adsorption and consecutive isomerization of olefinic bonds. In the study of octadecatrienoic acid (C18:3–9c, 12c, 15c) reactivity, Wolff [12] showed that *cis/trans* isomers, formed

during partial hydrogenation of oils, had a ratio that varied with initial oil composition, catalyst nature, and temperature. Isomerization also occurred on metal catalysts (e.g. Ni, Pd, Pt, Ru, and Rh), due to the formation of an intermediate compound allowing free rotation of the C=C bond [13–18]. Isomerization of methyl *cis*-9-octadecenoate (*cis* isomer) to methyl *trans*-9-octadecenoate (*trans* isomer) was studied in the presence of CoSn/ZnO catalysts under hydrogen pressure showing that the *cis-trans* isomerization was strongly influenced by the nature of catalytic sites [19].

Trans fatty acids have adverse health implications. The Food and Drug Administration (FDA) ruled that, as from January 1st 2006, nutrition labels for all conventional foods and supplements must indicate *trans*-fatty acid content [20]. Studies are still needed in order to satisfy the new specifications of a lower *trans*-isomer concentration in favor of a *cis*-isomer concentration.

The objective of the present work is to study the adsorption of *cis*-oleic acid on Ni(1 1 1) surface. *Cis*-Oleic acid (*cis*-9-octadecenoic acid: OA) is a monounsaturated omega-9 fatty acid, which means it has only one double bond between the carbons. It is a common fatty acid found in most animal and vegetable fats and is used in pharmaceuticals, medicine, and novel electronic applications, such as optoelectronic devices, sensors, field effect transistors, and dielectrics [21,22].

The adsorption of *cis*-oleic acid on nickel surfaces is a key step in several catalytic reactions. The most extensively used category of metal catalysts for hydrogenation of vegetable oils is nickel, due to its high activity, selectivity, low cost, and easy removal from oil after reaction [23,24]. Identification of active sites and their associated energy is important in heterogeneous catalytic reactions. Due to the complexity of the system, there is lack of information on oleic

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acid adsorption on active sites and electronic structure and bonding considerations related to the adsorption process. This study is still under discussion and a detailed analysis will be very promising for optimizing the industrial process. On the other hand, the difficulty to carry out experimental studies at molecular level make computer calculations a suitable tool to deal with this system. Theory and model are considered in the next section.

2. Theoretical method and adsorption model

Geometric optimization of *cis*-oleic acid on Ni(1 1 1) was carried out using the ASE method. In this quantum chemical technique, an Extended Hückel (EH)-like Hamiltonian is used for the calculation of valence electron eigen-energies. The main modification is the substitution of the Wolfsberg–Helmholtz constant for off-diagonal elements by a distance dependent expression [25]. In addition, a pairwise repulsive term is included so as to take into account the repulsive interaction between screened cores, thus allowing determination of equilibrium geometries for the adsorbed species. This formulation that can be rationalized applying the Hellmann–Feynman theorem [25] has been successfully employed for CO and hydrocarbon adsorption on a series of pure transition metals and intermetallics [10,26,27].

We have modeled the system using a two dimensional slab of finite thickness, so as to better simulate the semi-infinite nature of the metallic surface. A five-layer slab was employed as a compromise between computational economy and reasonable accuracy. Only the first three layers of the slab were allowed to relax. We started with a Ni lattice constant of $a_0 = 3.473 \text{ \AA}$. The molecule was adsorbed on one side of the slab and no lateral interactions were considered due to the diluted overlayer used. The total number of atoms in the OA molecule is 54 and we adopted an initial structure as the one reported by Misra et al. [28]. During calculations, the structures of both the molecule and the substrate were optimized at steps of 0.02 \AA and at an energy convergence of 0.01 eV . A schematic top view of the OA optimized structure adsorbed on Ni(1 1 1) is shown in Fig. 1(a). The OA molecule can be considered as made up of two parts which are separated by a C=C. One part of the molecule presents a carboxylic group (–COOH) as terminal group (carboxyl-sided chain) while the other part ends with a methyl group (methyl-sided chain). Both parts are formed by seven –CH₂– groups. During optimization, the molecule is adsorbed on the Ni surface adopting a bending configuration (Fig. 1(b)). Our theoretical calculations indicate that an energy difference favors a nonplanar form. This is in agreement with the structure adopted for the oleic acid molecule according to *cis* configuration [28]. Fig. 2 shows the four sites examined for the *cis*-oleic acid horizontal adsorption on Ni(1 1 1) surface, designated in order of increasing coordination number: on top (1C), bridge (2C), hcp (3CO), and fcc (3CT). On the other hand, the oleic acid molecule also has the possibility of being adsorbed on the nickel surface through the carboxylic group to the unsaturated oleic acid instead of through the double bond. In order to check competitive adsorption of –COOH and C=C bonds, we have also considered the vertical adsorption of the oleic acid on Ni(1 1 1) surface.

Adsorption energy (E_{ads}) values reported in Section 3 were calculated by the following total energy difference:

$$E_{\text{ads}} = E_{\text{T}}(\text{OA}/\text{Ni}(1\ 1\ 1)) - E_{\text{T}}(\text{OA}) - E_{\text{T}}(\text{Ni}(1\ 1\ 1)) \quad (1)$$

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

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

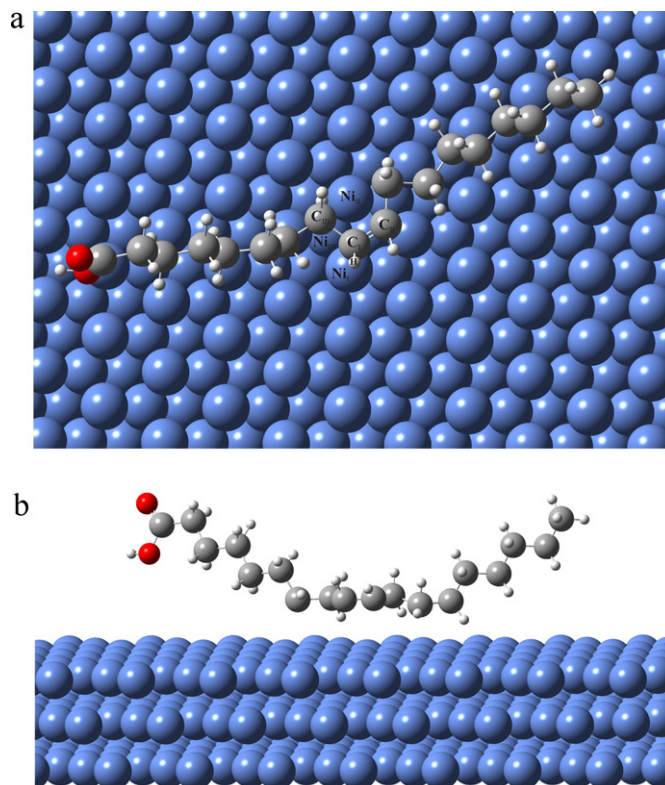


Fig. 1. Schematic top (a) and (b) lateral views for *cis*-C₁₇H₃₃COOH adsorption on Ni(1 1 1) surface. Ni \bullet ; C \bullet ; H \circ ; O \bullet . The double bond is located between C₁ and C₁₁.

Our calculations were implemented with the YAeHMOP package [29,30]. This method properly captures essential orbital interactions in chemisorption.

3. Results and discussion

Let us first consider the parallel adsorption of *cis*-oleic acid on the Ni(1 1 1) surface. The plots corresponding to adsorption energies are shown in Fig. 3. It can be observed that the energy curves for the four possible sites for molecular horizontal adsorption (Fig. 3(a)–(d)) are different and present well-defined minima. The latter indicates the presence of a strong bonding to the surface. The preferred site for the double bond C=C adsorption on Ni(1 1 1) is the three-fold octahedral, 3CO, with an equilibrium height of 1.10 \AA . The preferential site for adsorption is reasonable taking into account that the molecule is near the surface and, hence, it is influenced by its geometric details. On the other hand, the oleic acid molecule can also be adsorbed on the surface through the carboxylic group (see Fig. 4(a)). In order to check a possible competitive adsorption of –COOH and C=C groups, we also considered a vertical adsorption of the oleic acid on the Ni(1 1 1) surface. Fig. 4(b) shows the corresponding adiabatic energy curve. It can be seen that COOH is adsorbed at 1.7 \AA from the surface, with a less favorable adsorption energy when compared with C=C, thus corroborating that parallel adsorption through C=C bond dominates the adsorption process. However, in the last decades, competitive hydrogenation of C=O and C=C bonds has been the subject of several studies and it is still considered a challenging task, since hydrogenation of the C=C bond on metallic catalysts is normally much faster than that of the C=O bond. Selective hydrogenation of the oleic acid and/or of its esters to the unsaturated alcohols is, thus, a problem of selective hydrogenation of –COOH in presence of the C=C double bond [31].

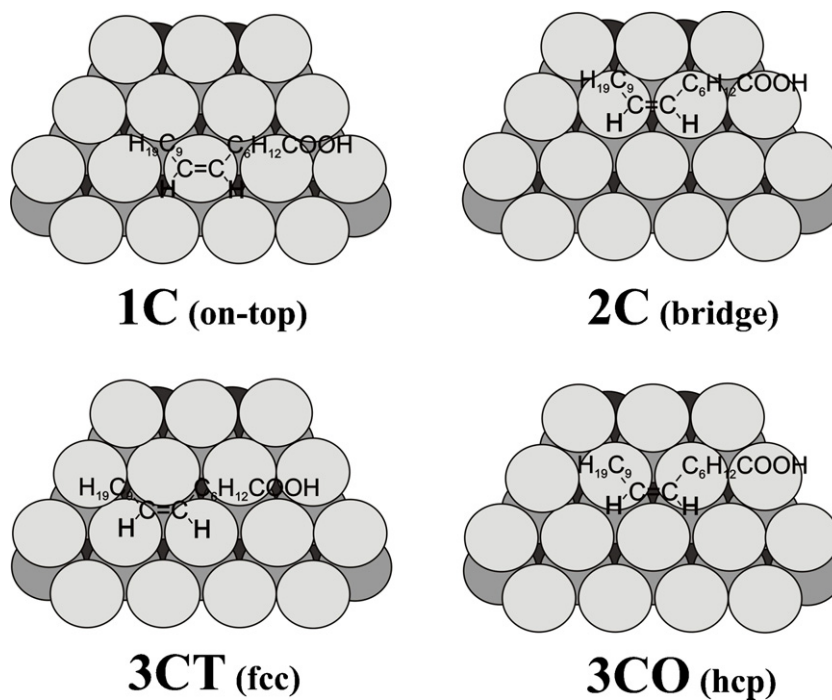


Fig. 2. Adsorption sites for *cis*-C₁₇H₃₃COOH on Ni(111).

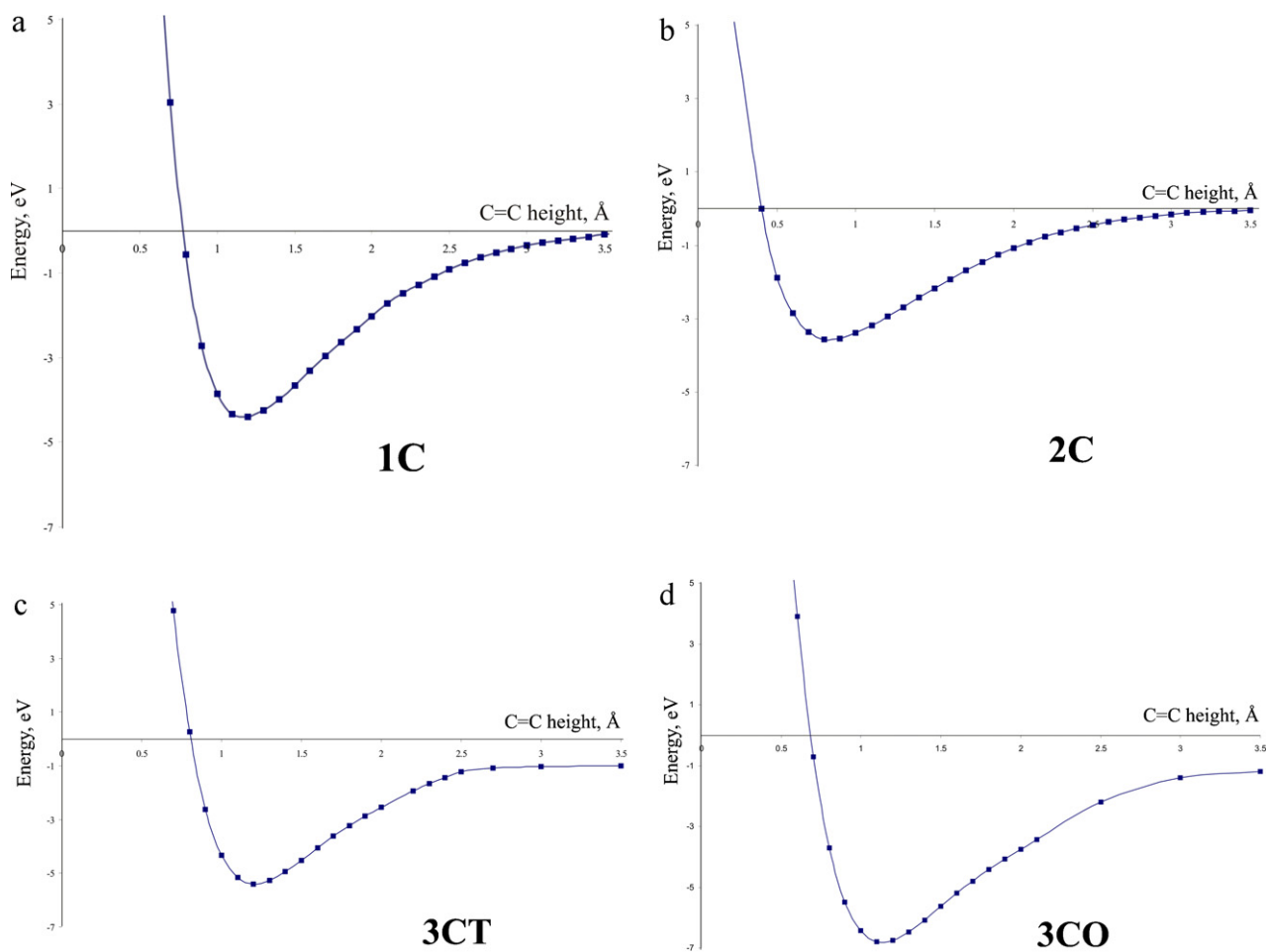


Fig. 3. Adiabatic energy curves for the different adsorption sites of *cis*-C₁₇H₃₃COOH on Ni(111) surface.

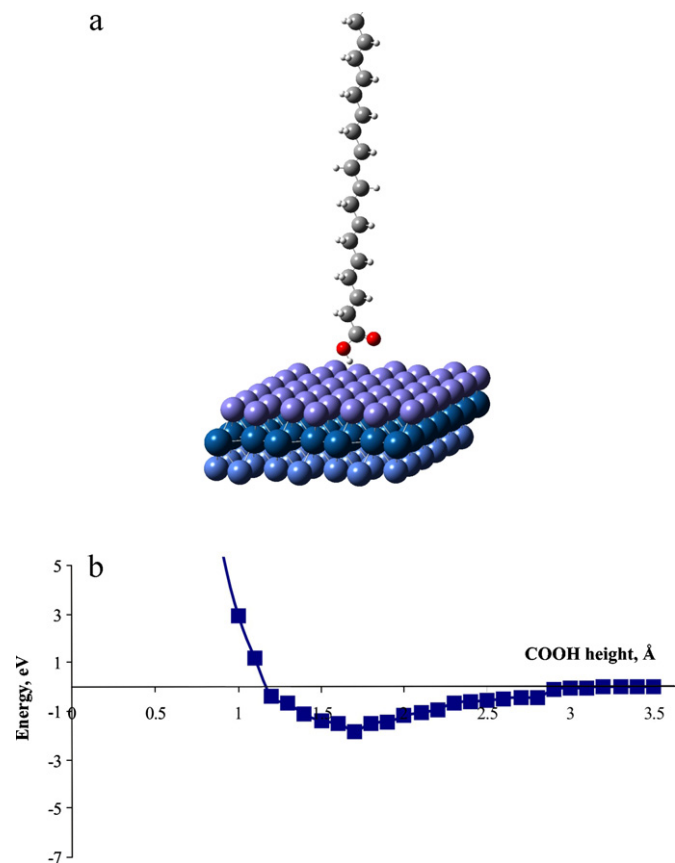


Fig. 4. (a) Schematic lateral view for the *cis*-C₁₇H₃₃COOH vertical adsorption on the Ni(1 1 1) surface. (b) Adiabatic energy curves (eV) vs. COOH/surface distance (Å) for *cis*-C₁₇H₃₃COOH adsorption on Ni(1 1 1) surface.

In order to analyze electronic interactions, the molecule was placed in the three-fold octahedral site (3CO), in the preferential adsorption site. The DOS that a two-dimensional monolayer of the *cis*-oleic acid, arranged in the same geometry as the molecules takes on the surface, is shown in Fig. 5(c). The DOS is similar to that of the isolated molecule; however, all molecular orbitals are located at lower energy values compared to the isolated species which represent an energetic stabilization of the monolayer after adsorption. We can see that the bands corresponding to *cis*-oleic acid spread out, after adsorption on the metal surface. The lowest p orbital of the molecule substantially interacts with metal orbitals; the DOS

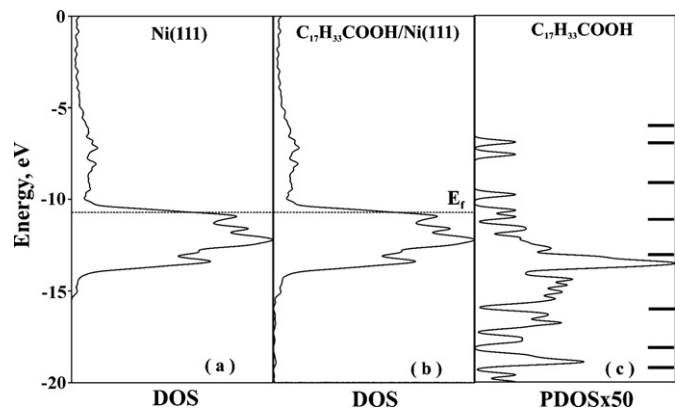


Fig. 5. (a) DOS for the Ni(111) isolated system, (b) DOS for the *cis*-C₁₇H₃₃COOH/Ni(111) system and (c) projected DOS for the *cis*-C₁₇H₃₃COOH molecule adsorbed on the Ni(1 1 1) surface. The horizontal thick lines to the right indicate the orbital locations in the isolated *cis*-C₁₇H₃₃COOH molecule.

molecule is pushed up above the Fermi level and the main body of the band is pushed down. This means that electron transfer between the molecule and the surface has occurred and that the molecule is interacting with the surface. On the left, in Fig. 5(a), the DOS of the bare neutral Ni(1 1 1) surface slab model is presented. Above -15 eV a broad region can be seen due to the d orbitals from the Ni slab. In this region there are contributions from frontier orbitals. Fermi level position shows that most of the d band is filled. 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 [27,32,33]. The dispersion of the s and p bands is much larger than the d band, thus indicating the much more contracted nature of d orbitals. The surface-layer of the slab is negatively charged with regard to the bulk due to the finite size of the slab. The DOS of the chemisorbed system *cis*-oleic acid on Ni(1 1 1) is displayed in Fig. 5(b). The Fermi energy of the metal surface moves slightly, because of the finite thickness of the slab and an electron transfer between the slab and the adsorbate. The system's DOS nearby the Fermi energy (E_f) is dominated by the nickel substrate. At lower energies the DOS is modified by the adsorbed molecule. The maximum of the Ni d density lies just at the HOMO level of the oleic acid molecule thus explaining the electronic interaction. It is evident that the HOMO and the LUMO of the molecule are dispersed (see Fig. 5(c)), which is also indicative of molecule–surface interaction. Almost all molecular orbitals interact with the metal surface, except for those lying lower in energy. During adsorption, a mixing of σ and π orbitals takes place. The bending of the molecule out of the C=C plane is traced to π interactions and reorientation of the frontier orbitals for a better overlap in the molecular complex. Once the molecule is adsorbed on Ni(1 1 1) and the geometry optimized, the lowest energy is also achieved with a bending of the molecule away from the surface. The σ orbitals of the molecule are involved in bonding to the surface, this shows up in band dispersion and electronic structure changes.

The results in Table 1 show that the charge transfer between the substrate and the adsorbate mainly comes from the interface between C=C and their neighboring C–C and C–H bonds and Ni atoms from the adsorption site. There is no interaction between molecule and surface other than at the bonding site. As it can be seen in Fig. 1(b), the *cis*-oleic acid is adsorbed in the 3CO site with its carbon double bond located over three Ni atoms. 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 bonding interaction between molecule and substrate is analyzed considering COOP curves for Ni–Ni, C=C, C–C, and C–H bonds before and after adsorption (see Figs. 6 and 7). These curves and the computed overlap population (OP) values change after adsorption. The curves present bonding and antibonding peaks below the Fermi Energy level (E_f). Integration up to the Fermi level gives the total OP for the bondings. If we compare the corresponding curves in Fig. 6, a smaller OP is observed after adsorption, thus indicating that there is a weakening of the C=C, C–C, and C–H bonds that participate in the molecule–surface bonding. Fig. 7 also shows a decrease in the PDOS at E_f for the neighboring Ni atoms, in comparison to the calculated DOS for the clean system. This means that electrons are transferred to some deeper energy level in the valence band and participate in the bonding with molecular orbitals. Ni–Ni antibonding states are now populated and this changes the E_f with respect to the bare surface. There is less metal–metal bonding due to participation of Ni p and d orbitals in surface–molecule bondings. Computed OP values between atoms are shown in Table 1 (see *cis*-oleic acid atom numbering in Fig. 1(b)). C=C and C–C OPs decrease nearly 12% and 11% respectively after adsorption. C–H bonds do not suffer significant changes, they only decrease a 2%, thus indicating that there is

Table 1
Orbital occupations, net charges and overlap population (OP) for the atoms that participate in the interactions.

Atom	Orbital occupation			Charge	Bond	OP
	s	p	d			
C _I	0.9979	2.6458		0.3563 ^a	C _I =C _{II}	1.034 ^a
	1.0005	3.1419		-0.1423 ^b		1.170 ^b
C _{II}	0.9886	2.5071		0.5044 ^a	C _I -C _{III}	0.744 ^a
	0.9944	3.0837		-0.0782 ^b		0.834 ^b
C _{III}	0.9563	2.6006		0.4431 ^a	C _I -H _I	0.848 ^a
	0.9536	2.9030		0.1433 ^b		0.867 ^b
H _I	0.9359			0.0641 ^a	Ni _I -Ni _{II}	0.200 ^a
Ni _I	0.9483			0.0517 ^b	Ni _I -Ni _{III}	0.220 ^b
	0.6378	0.4124	8.8514	0.0983 ^a		0.165 ^a
Ni _{II}	0.6592	0.4184	8.8537	0.0687 ^b	Ni _I -C _I	0.162 ^b
	0.6148	0.3791	8.7856	0.2205 ^a		0.047 ^a
Ni _{III}	0.6592	0.4184	8.8537	0.0687 ^b	Ni _I -H _I	0.009 ^a
	0.6062	0.4167	8.2830	0.6941 ^a		
	0.6012	0.4177	8.3139	0.6672 ^b		

Ni_{II}, Ni_{III}: nearest neighbors to Ni_I corresponding to the first and the second close-packed fcc (1 1 1) plane, respectively.

^a C₁₇H₃₃COOH/Ni(1 1 1) system.

^b Isolated C₁₇H₃₃COOH or isolated Ni(1 1 1) surface.

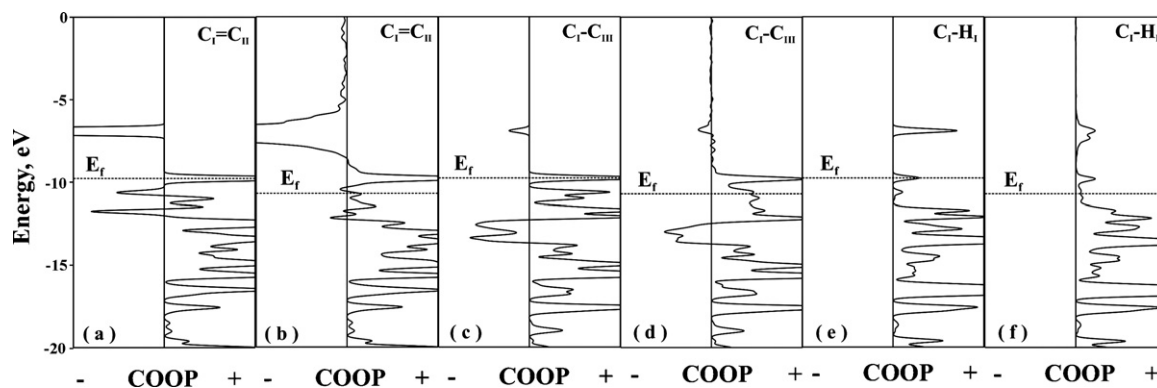


Fig. 6. COOP curves for the C=C bond (a) before and (b) after adsorption. COOP curves for the C-C bond (c) before and (d) after adsorption. COOP curves for the C-H bond (e) before and (f) after adsorption.

a slight weakening in the C-H bond. A large bonding OP between C and Ni atoms appears, while the Ni-Ni OP decreases, this indicates that the adsorbate-surface bonding requires that mainly C=C, C-C, and Ni-Ni bonding decrease. The Ni_I-Ni_{II} OP decreases a 9% while the Ni_I-Ni_{III} OP decreases less than 2% (see Fig. 7). This indicates that the new interactions mainly affect the strength of neighboring Ni-Ni bonds. Changes in Ni-Ni bonds corresponding to the second slab layer are subtle.

The bond that significantly contributes to *cis*-oleic acid adsorption is the Ni-C interaction (see Table 1). On the other hand, a Ni-H

interaction can be seen but it presents a very small overlap population. In order to study the bonding in detail, we have plotted COOP curves for Ni-C and Ni-H bonds in Fig. 8. We can appreciate the Ni-C contribution to the molecule-surface bonding. The smaller Ni-H interaction could indicate that the hydrogenolysis of the molecule is not being promoted. This condition is desired for the hydrogenation process of industrial oils.

Orbital by orbital contributions to molecule-metal chemisorption (see orbital occupation in Table 1) mainly correspond to C_I p_x and p_y orbitals (populations increase 34% and 10% respectively), C_{II}

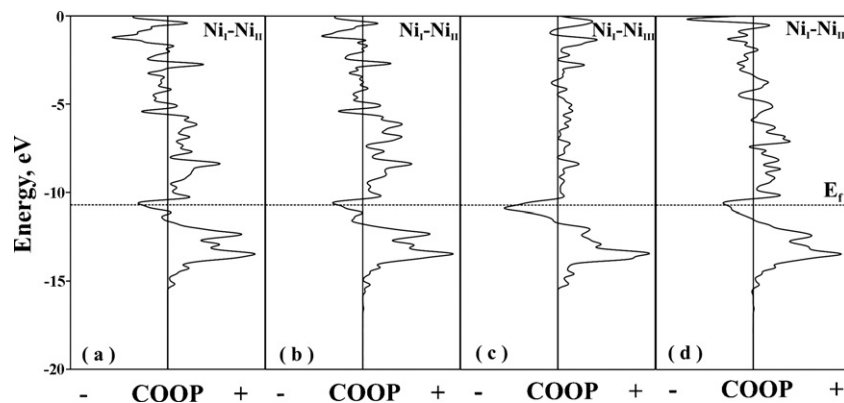


Fig. 7. COOP curves for the Ni_I-Ni_{II} bond (a) before and (b) after adsorption. COOP curves for the Ni_I-Ni_{III} bond (c) before and (d) after adsorption.

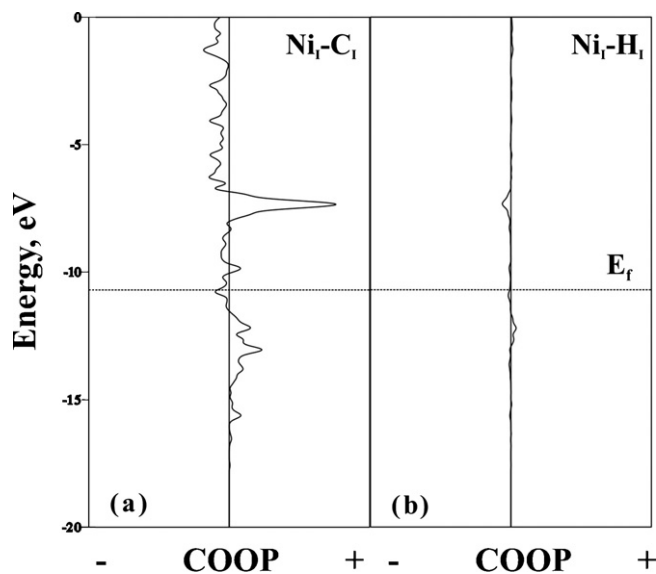


Fig. 8. COOP curves for (a) Ni–C and (b) Ni–H interactions.

and C_{III} p_x orbitals (populations increase 42% and 21% respectively) overlapping with Ni_I and Ni_{II} p_x , p_z and d_z^2 orbitals (populations change 10%, 13%, and 5% (for Ni_I) and 35%, 5%, and 2% (for Ni_{II})) and Ni_{III} d_{yz} orbital (populations increase 2%). It is reasonable for d orbitals to be involved in surface bonding since the role of d states is critical in defining adsorption site and adsorption geometry. A bonding between C and metal arises because of the closeness of C valence levels to s–d band of Ni states and because of the availability of C 2p orbitals for better bonding interactions with metallic d orbitals. This is in agreement with the expectation that carbon p orbitals should play a major role in bordering molecular orbitals. The lobes of these orbitals are well-oriented and have the possibility of overlapping with metal orbitals.

4. Conclusions

The theoretical study of the *cis*-oleic acid adsorbed on Ni(111) has been performed by means of ASED calculations. Competitive adsorption analysis of the C=C bond vs. the C=O bond proved that horizontal adsorption dominates the adsorption process. The electronic properties of the molecule in the region close to the double bond are modified, while the adsorption energy depends on the adsorption site coordination number. The adsorption with the center of the double carbon bond placed above the 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 mainly because a bonding between carbons from the double bond

and the nickel surface remains. The main interaction comes from Ni p and Ni d that are involved in the bonding with the C p orbitals. A small Ni–H interaction is also detected.

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