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Selectivity of Pd-Functionalized PtNi(111) Surface: *cis*-3-Hexenoic Acid Adsorption

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Abstract Vienna Ab-initio Simulation Package (VASP) is employed to study the adsorption of the monounsaturated *cis*-3-hexenoic acid (*cis*-C_5H_9COOH) on a bimetallic surface compound of a Pd-functionalized layer of Pt on Ni(111). The *cis*-3-hexenoic acid is much distorted on Pt than Pd surface atoms. The molecule interacts through the C=C bond but also presents an important contact via the COOH group; consequently, the carboxyl group results partial dissociate. In addition, Pd favors H removal. The surface-molecule interaction is most stable on Pd-functionalized PtNi(111) (−6.36 eV) than unfunctionalized PtNi(111) (−2.40 eV). Calculations show that Pd atoms stabilize the π modes better than Pt. The overall adsorption energy is a compromise between the distortion energy of the molecule on Pt atoms and the stabilization due to the interaction between the molecule and Pd surface atoms.

Graphical Abstract
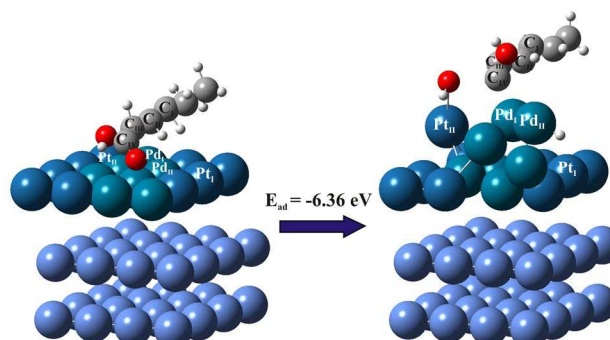
Keywords Catalysis · Adsorption · Elementary Kinetics · Computational chemistry · Theory, DFT · Theory

1 Introduction

A few years ago, *trans* and saturated fats have been shown to be harmful for the organism [1–3] whereas *cis* and monounsaturated fatty acids seem to be able to reduce the bad cholesterol in the blood [4]. There is still fewer formation of *cis* isomers during the process, mainly when nickel catalysts are used because of isomerization or migration of double bonds [5–7]. One way to improve the reaction yield is modifying nickel catalyst via promoters which increase the activity and selectivity to the required products. Pd and Pt atoms present high activity and can operate at lower reaction temperatures (80–120 °C) than Ni [8]; these characteristics make them promising promoters for oil processing.

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2 Theory and Model

The density functional theory (DFT) is employed to study the adsorption of a monounsaturated organic molecule, the *cis*-3-hexenoic acid (*cis*-C_5H_9COOH) on a surface compound of one Pd-functionalized layer of Pt on Ni(111) surface. The Vienna Ab-initio Simulation Package (VASP) was using to perform the calculations [9, 10]. In this code plane wave basis sets are applied to resolve the Kohn-Sham equations. The electron projector augmented wave (PAW) method and the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) functional were employed [11–16]. The fixed convergence of the plane-wave expansion was obtained with cut-off energy of 450 eV. A set of $3 \times 3 \times 1$ Monkhorst-Pack k-points was used to sample the Brillouin Zone [17]. The ground state was found by a Methfessel-Paxton smearing of 0.2 eV [18]. In order to evaluate the magnetic properties of the systems, the calculations were performed at the spin polarization level.

3 Results and Discussion

First, we have optimized the geometry of the gas phase of the *cis*-3-hexenoic acid molecule. The results for the isolated molecule are close to those of experimental and previous theoretical studies [19]. Our calculations predicted C=C and C–C distances of 1.34 and 1.54 Å respectively. This values are similar to the usual bond distances for the ethene molecule in experimental [20] and theoretical [21, 22] studies. Then, we have modeled the bimetallic surface of one layer of Pt(111) on top of four Ni(111) layers within the three-dimensionally periodic supercell. Therefore, the Pt layer was functionalized with Pd atoms through partial substitution. The two bottom layers of the slab are kept fixed in bulk positions to represent the semi-infinite bulk crystal beneath the surface and the rest of the layers were relaxed. Finally, we have explored the molecule absorption on the surface. The initial geometry can be seen in Fig. 1a. The molecule is allowed to relax together with the top three layers of 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 final geometry is showed in Fig. 1b. The Pd atoms behind the molecule move from their lattice original position and it rearranges as consequence of the strong interaction. The *cis*-3-hexenoic acid interacts with the surface through its C=C bond while the carbon chain is parallel to the metallic surface. The main skeleton of the molecule is sited on Pd atoms while the molecule extremes are located on Pt atoms (see Fig. 2). It is observed that the molecule is much distorted on the Pt than Pd surface atoms and consequently its geometry
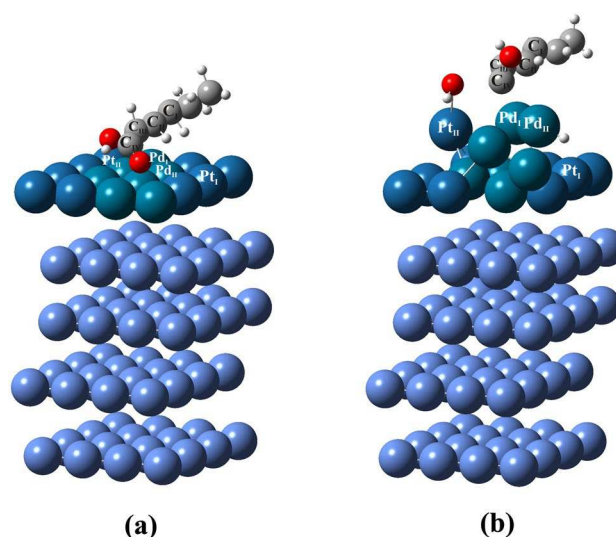

Fig. 1 Initial (**a**) and final (**b**) geometries for *cis*-3-hexenoic acid adsorbed on Pd-functionalized PtNi(111) surface
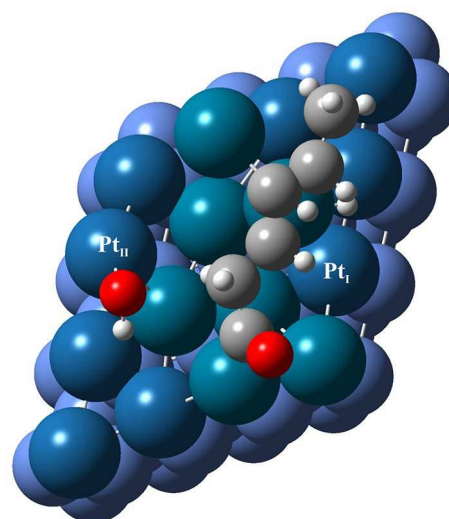

Fig. 2 Top view of the *cis*-3-hexenoic acid adsorbed on Pd-functionalized PtNi(111) surface

experiments more changes comparing to the gas phase. In the resulting geometry, the C=C lies on neighboring two Pd atoms. The new Pd–C interactions are 2.79 and 2.99 Å respectively, which are according to the normal range for organometallic complexes [23]. The changes on C–C bond length can be used as a measure of the activation of the adsorbed molecule. We found that the C–C bond is shortened with respect to the gas phase and it is in relation to the strong adsorption. The C=C and nearest C-C bond contract to 1.20 and 1.30 Å, respectively.

The molecule interacts with the surface through the double carbon bond but also presents an important contact via
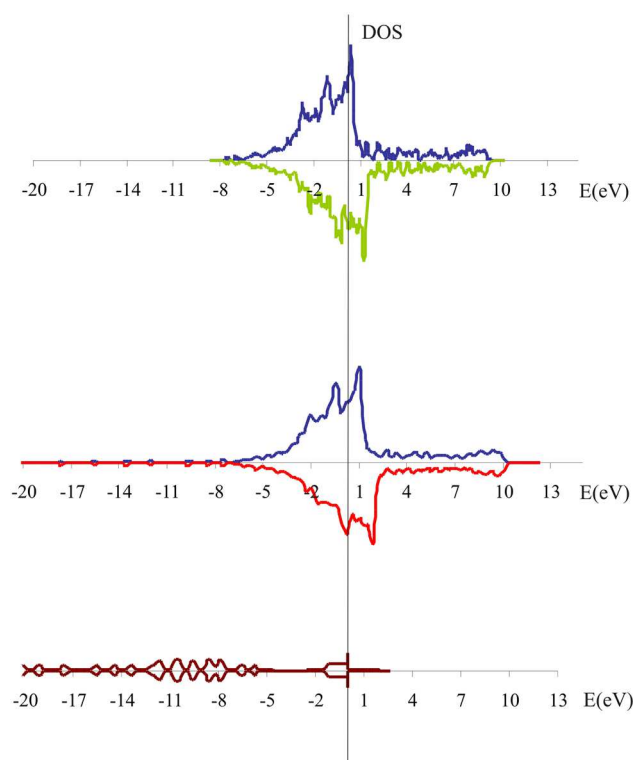
Table 1 Electronic charge of atoms that participate in the interactions

Atom	Electron charge		
	s	p	d
C_I	0.829	1.761[a]	
	0.825	1.803[b]	
C_{II}	0.845	1.709[a]	
	0.853	1.767[b]	
C_{III}	0.850	1.702[a]	
	0.819	1.779[b]	
C_{IV}	0.832	1.823[a]	
	0.823	1.790[b]	
Pt_I	0.630	0.547	7.729[a]
	0.664	0.517	7.769[b]
Pt_{II}	0.570	0.337	7.668[a]
	0.673	0.505	7.788[b]
Pd_I	0.364	0.527	7.989[a]
	0.411	0.311	7.995[b]
Pd_{II}	0.310	0.293	7.983[a]
	0.387	0.294	8.002[b]

[a] After adsorption

[b] Before adsorption

Fig. 3 Density of states (DOS) for (**a**) the clean Pd-functionalized PtNi(111) surface, (**b**) *cis*-3-hexenoic acid adsorbed on Pd-functionalized PtNi(111) surface and (**c**) the isolated *cis*-3-hexenoic acid molecule

the COOH group. Consequently, the carboxyl group results partial dissociate: the OH is separated of the molecule and interacts with a Pt atom (Pt-OH distance = 2.50 Å). On the other hand, the C-C bond (near neighbor to the double bond) loses a hydrogen atom that interacts with both, a Pt atom (Pt-H distance = 1.32 Å) and a Pd atom of the surface (Pd-H = 1.42 Å). In previos work, we have corroborated that the PtNi(111) surface is active to the *cis*-3-hexenoic conversion from the unsaturated acid to unsaturated alcohol [19]. We can now confirm that Pd change the selectivity of the PtNi(111) surface. On the other hand, our study shows that the Pd-functionalized PtNi(111) surface favors H (or water) removal.

The binding energy is -6.36 eV. The surface-molecule interaction is most stable on Pd-functionalized PtNi(111) than unfunctionalized PtNi(111) (−2.40 eV [19]). Calculations show that the Pd atoms clearly stabilize the π modes better than Pt. To explain the adsorption strength and the geometry difference, the adsorption energy can be divided into its main components. When the molecule interacts with the metallic surface, new bonds are created and the geometry of the molecule and the surface changes. The adsorption energy is therefore partitioned into the distortion energy of the molecule, the distortion energy of the surface (a minor contribution) and the interaction energy between the molecule and the surface. On Pt atoms, the stronger distortion of the molecule led to a higher energy cost to reach the adsorption geometry.

The molecular distortion favors the interaction between the molecule and the surface. Adsorption is favored on the metallic surface because the bonding of the π states with the metals d-band, the interaction mainly takes place between C p and Pt Ni metals d band. The interaction takes also place between C p and the s p orbitals of Pt and Pd atoms (see Table 1; Fig. 3). Pt drives to an effective interaction with a strong molecular distortion, while Pd is the case of a weaker interaction with an overall adsorption that is less distorted. The weaker distortion of the ethylene molecule on Pd(111) than Pt(111) has been observed in calculations by Sautet and co-workers [24]. The adsorbate metal overlap is larger for Pt because the d states are more expanded but the stabilization due to molecule-surface interaction was greater on the Pd promoted surface than unfuctionalized surface. Finally, the overall adsorption energy is a compromise between the distortion energy of the molecule on Pt atoms and the stabilization due to the interaction between the molecule and Pd atoms of surface.

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