

## 2nd World Congress and Expo on Nanotechnology and Material Science April 04-06, 2016 at Dubai, UAE

### PtNi(111) catalyst: DFT study of unsaturated organic acid conversion to alcohol

E. Diez Tortorella<sup>1</sup>, S. Ulacco<sup>1</sup> and Sandra Simonetti<sup>2</sup>

<sup>1</sup> Universidad Tecnológica Nacional (UTN), Bahía Blanca, Argentina

<sup>2</sup> Universidad Nacional del Sur (UNS)- CONICET, Bahía Blanca, Argentina

The interest in analyzing the bimetallic substrates in molecule/catalyst interfaces is to show their influence in the absorption and the corresponding chemical and geometrical effects. Specifically, 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 this work, we use the Vienna Ab initio simulation package (VASP) to study bimetallic surface compounds of a monolayer of Pt on Ni(111) and their interaction with an organic acid molecule, the cis-3-hexenoic acid. A previous 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.

We have modeled the bimetallic surface of one layer of Pt on top of four Ni(111) layers within the three-dimensionally periodic supercell. The bottom two layers of the PtNi(111) 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 have placed it in a 20 Å cubic box. Highly symmetrical boxes can produce wrong orbital occupancies for the isolated molecule. We have explored the molecule absorption on the surface with a 3x3x1 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 relaxed layers are below 0.01 eV/Å, the structural relaxation is stopped.

In order to analyze absorption, we have considered several possible configurations for C<sub>5</sub>H<sub>9</sub>COOH absorption above the bimetallic PtNi(111) surface; after system relaxation, we have selected for the present study the most stable geometry, it can be seen in Fig. 1. Their complete molecular structure interacts with the bimetallic surface and the absorption results to be strong; we have obtained an optimum energy of -2.4 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(111) induces the conversion from the unsaturated acid to the unsaturated alcohol. 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(111) surface preserves intact the double bond of the adsorbed molecule and the dehydrogenation of the double bond is not observed.

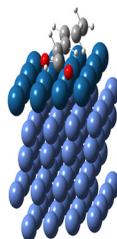


Fig. 1. Schematic view of cis-3-hexenoic acid adsorption on the PtNi(111) surface.