Glycerol adsorption energy onto Pt and PtSn (001) surfaces using density functional theory and vdW corrections

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Abstract: Glycerol is a versatile molecule because of its wide applicability, one of them is its use as fuel in fuel cells, since glycerol has a reliable energy density and reversible efficiency [1]. However, the oxidation of alcohols into fuel cells is one of the major challenges of these systems [2-5]. Computational theoretical studies have been carried out for a better understanding of the oxidation of electrochemical process [6]. This work deals with the glycerol adsorption of on the surfaces of Pt and PtSn by computational calculations based in Density Functional Theory (DFT) [7,8]. The calculations were performed using Quantum Espresso program [9]. Exchange and correlation energies were determined using Perdew−Burke−Ernzerhof (PBE) [10] form of the generalized gradient approximation (GGA). The energy cutoff for the wave-function is 25 Ry (340 eV). Ultrasoft pseudopotentials [11] and a 6x6x1 Monkhost-Pack k-point mesh were used. A Marzari-Vanderbilt smearing of 0.2 eV was applied. A 2x2x1 slab with three layers was created for each metal surface all of them kept the Pt-botton layer freeze according to the Pt unit cell lattice parameter. Studies shown that glycerol has several conformers [12], then the three lower energy conformers were used to add it over the surfaces in this work. Van der Waals (vdW) corrections (DFT-D2) [13] were also included to study the effects of long range interactions. The results (see Figure 1 and Table 1) show that for the Pt and PtSn, both in plane 001, the lower energy configurations with van der Waals correction presented lower energy than those without this correction and in both cases, the configuration of the highest energy was the 3d configuration in which only one O atom of glycerol is pointed to the surface and the other two are in the opposite direction. Through the theoretical data, it was observed that the glycerol molecule interacts with the atoms of the surfaces of the metals principally via M-O, as already mentioned in the literature [14-16], since the states of greater contributions coming from the oxygen atoms overlap the *d*-states of the metals. With the exception of conformer 2, the other two conformers presented configurations with the lowest energy coming from the surface with the three oxygen atoms of the glycerol molecule. Thus, this work re-affirms the idea that the molecule adsorb on the surface of transition metals via M-O bonding, besides, changes in the adsorption energy of the glycerol configurations occurred with the addition of Sn in the structure of Pt. The van der Waals correction led to configurations of the lower energy glycerol on both Pt and PtSn surfaces.
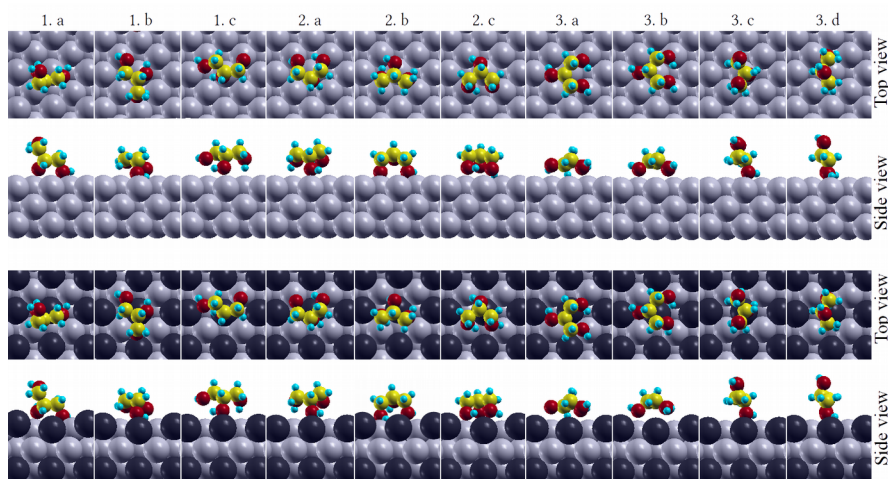
Figure 1: Configurations of glycerol on Pt and PtSn surfaces.

Table 1: Energies of glycerol adsorption for configurations.

Configurações	1a	1b	1c	2a	2b	2c	3a	3b	3c	3d
$E_{ads}^{gly/Pt}$ (eV)	-0,94	-1,06	-1,66	-1,64	-1,24	-1,16	-1,07	-1,07	-0,31	-0,86
$E_{ads}^{gly/PtSn}$ (eV)	-1,99	-2,68	-2,48	-2,18	-2,85	-2,32	-2,71	-2,70	-1,32	-1,85
$E_{ads}^{gly/Pt}$ (eV) - DFT-D2	-0,68	-1,49	-1,49	-1,82	-1,08	-1,61	-0,74	-1,20	-0,52	-0,58
$E_{ads}^{gly/PtSn}$ (eV) - DFT-D2	-2,20	-2,91	-2,45	-2,86	-3,17	-3,09	-2,24	-2,36	-1,27	-1,80

Key-words: DFT, glycerol, Pt and PtSn, van der Waals corrections

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References:

[1] B. Katryniok, et al. Green Chem., 13, 1960 (2011).

[2] Z. Zhang, et al. J. Hydrogen Energy, 37, 9393 (2012).

[3] A. Falase, et al. Electrochim. Acta, 66, 295 (2012).

[4] P. S. Fernández, et al. Electrochim. Acta, 66, 180 (2012).

[5] J. F. Gomes, G. Tremiliosi-Filho. Electrocatal., 2, 96 (2011).

[6] B. Braunchweig, et al. Catal. Today, 202, 197 (2013).

[7] P. Hohenberg, W. Kohn. Phys. Rev., 136, B864 (1964).

[8] P. Giannozzi, et al. J. Phys.: Condens. Matter, 21, 395502 (2009).

[9] W. Kohn, L. J. Sham. Phys. Rev., 140, A1133 (1965).

[10] J. P. Perdew, et al. Phys. Rev. Letters, 77, 18, 3865 (1996).

[11] A. M. Rappe, et al. Phys. Rev. B, 41, 1227 (1990).

[12] C. S. Callam, et al. J. Am. Chem. Soc., 58, 11743 (2001).

[13] S. Grimme. J. Comput. Chem., 27, 1787 (2006).

[14] B. Liu, J. Greeley. Phys. Chem. Chem. Phys., 15, 6475 (2013).

[15] B. Liu, J Greeley. J. Phys. Chem. C, 115, 19702 (2011).

[16] P. Tereshchuk et al. J. Phys. Chem. C., 118, 15251 (2014).