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Molecular Modelling of Polyol Electro-Oxidation Reaction on Pt Surfaces

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Abstract: The Biomass is the most abundant renewable resource and an alternative to reduce the world dependence of Diesel Oil.[1,2] Brazil has 18% energy supply originated by sugar cane and it is one of the largest producers and consumers of Biodiesel in the world[3]; for these reasons, the efficient use of polyol, derivative from Biomass, like Glycerol, Erythritol, Xylitol, Arabitol, Sorbitol, and others, is essential.

The Polyol Electrooxidation Reaction (REOP) is an alternative because, through electrochemical techniques, products with higher value can be obtained from these Biomass derivatives. Prof. Pablo Fernández, with his electrocatalysis group, from Unicamp's Institute of Chemistry, has explored this reaction using a four carbons polyol, Erythritol, a common compound used as sweetener by the Food Industry.

There is a great lack of knowledge regarding the intermediates from REOP and studies aimed to understand the reaction mechanisms are necessary. The present work applies computational simulations based on Density Functional Theory (DFT), using the software VASP, to explore the interaction of multiple Erytritol intermediates with different platinum surfaces. The modeling helps to elucidate the details from the mechanisms and contributes to the understanding of the electrochemical results obtained.

First principles calculations based on periodic DFT have been performed to gain insight into the structural, energetic and electronic structure of five intermediates with two dehydrogenations, on three different platinum surfaces. Based on adsorption energy calculations, the intermediates were compared and the understanding of the abundance of intermediates and products on REOP was possible.

Intermediates with surface bonds through adjacent carbons were more unstable and disadvantaged; the fact was justified by the great tension created in the bonds and the lesser degree of freedom. The most favorable adsorption energies were found to those intermediates having bonds with two non-adjacent carbons; the possibility of a stronger interaction between the molecular chain and the surfaces was a favorable point for the systems stabilities.

The analysis of Electron Charge Differences showed a charge rearrangement between the dehydrogenated carbons and the Pt atoms, indicating bond between these atoms; with the PDOS analysis, the electronic nature of the bonds was explored. The

interactions occurred mainly between the Pt ‘d’ states and the C ‘p’ states. Further analyses were performed to understand the interactions between the hydroxyls and the surfaces; the PDOS profile showed stronger interactions between the same energy states as the carbons.

Key-words: Polyol Electro-oxidation, DFT, Simulation, Modelling, Adsorption Study.
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References:

[1] García-Muelas, R.; López, N.; J. *Phys. Chem. C*., **2014**, 118, 17531-17537.
[2] Ragauskasm, A. J.; Williams, C. K.; Davison, B. H.; Britovsek, G.; Cairney, J.; Eckert, C. A.; Frederick, W. J.; Hallett, J. P.; Leak, D. J.; Liotta, C. L.; et al. *Science* **2006**, 311, 484-489.
[3] Site da ANP - Agencia Nacional do Petróleo (http://www.anp.gov.br/).
[4] Dzade, N., Roldan, A., Leeuw, N., *Environ. Sci. Technol.*, **2017**, 51, 3461-3470.
[5] Chang, C., Liu, C., Wu, S., Tsai, M., *Phys. Chem. Chem. Phys.*, **2017**, 19, 4989-4996.
[6] Garcia, A. C.; Kolb, M. J.; Nierop y Sanchez C.; Vos, J.; Birdja, Y. Y.; Kwon, Y.; Tremiliosi-Filho, G.; Koper, M. T. M.; ACS Catal., **2016**, 6, 4491-4500
[7] Kwon, Y., de Jong, Ed., van der Waal, J.K., Koper, M.T.M., *ChemEletroChem*, accepted.