

# **Mechanisms of reactions on Pt nanoclusters used in electrocatalysis. The role of organic surfactants.**

S. Dobrin<sup>1</sup>, D. Mowbray<sup>1</sup>, J.K. Nørskov<sup>1</sup>, B.L. Abrams<sup>1</sup>, I. Chorkendorff<sup>1</sup>, E. Savinova<sup>2</sup>.

<sup>1</sup>*Department of Physics, Technical University of Denmark, DK-2800 Kongens Lyngby, Denmark*

<sup>2</sup>*LMSPC-UMR 7515 du CNRS-ULP-ECPM, 25, rue Becquerel, F 67087 Strasbourg Cedex 2, France*

*Sergey.Dobrin@fysik.dtu.dk*

Small Pt nanoclusters (<10nm) are widely used in catalysis and electrocatalysis. In particular, they are of interest in Hydrogen Evolution and Hydrogen Oxidation Reactions (HER/HOR) and in oxidation processes, such as CO and organic molecule oxidation. [1,2] The clusters can be synthesized by the modified inverse micelle [3] technique, which allows one to prepare clusters coated by organic surfactants and to control the size of the clusters. Chemical properties of the clusters depend upon their size and the properties of the surfactants. In spite of numerous studies, these effects are not fully understood yet.

In the current study we focus on the mechanisms of HER and CO oxidation reactions on the Pt nanoclusters, as well as on the mechanisms of attachment of the organic surfactants to the clusters. We also discuss the effect of the surfactants on the catalytic properties of the clusters. Our studies are based on electrochemical experiments and DFT modeling performed using plane wave DFT. Adsorption on the clusters has been modeled using DACAPO. [4]

In the case of Pt nanoclusters stabilized by a non-ionic surfactant, the HER activity has been found to be comparable to that of polycrystalline platinum catalyst. The negligible suppression of the HER indicates that the surfactants may not significantly block the active sites necessary for the HER. This experimental finding agrees with our computational results, which suggest that the surfactants attach preferentially to corner atoms of the clusters, thereby keeping facets of the clusters available for the HER or oxidation reactions.

Experimental studies show that in the case of Pt particles stabilized on carbon substrates the catalytic activity in CO monolayer oxidation decays systematically with the decrease of their size [5, 6]. We use our DFT calculations to model these experimental findings.

Results of this study are of interest for developing new catalysts, which can be used in heterogeneous catalysis, electrochemistry and fuel cells.

[1] J.K. Nørskov, et al., "Trends in the Exchange Current for Hydrogen Evolution" *J. Electrochem. Soc.* (152), J23 (2005).

[2] Greeley, J., et al., "Computational High-Throughput Screening of Electrocatalytic materials for Hydrogen Evolution", *Nature Materials*, **5**, 909-913 (2006).

[3] Wilcoxon, J.P.; Abrams, B.L., "Synthesis, Structure and Properties of Metal Nanoclusters" *Chemical Society Reviews*, **35**, 1162-1194 (2006).

[4] <http://dcwww.camd.dtu.dk/campos/Dacapo/>

[5] O. V. Cherstiouk, P. A. Simonov and E. R. Savinova, *Electrochim. Acta.* **48** (2003) 3851-3860.

[6] F. Maillard, M. Eikerling, O.V. Cherstiouk, S. Schreiber, E. Savinova, and U. Stimming, *Faraday Discussions* **125** (2004) 357-377.