Quantum-chemical modeling of binary nanoclusters of platinum in the environment of low temperature fuel cells

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The aim of the work was to simulate and calculate interaction of platinum binary nanoclusters Pt_nX_m (X – transition metals Cr, Fe, Co, Ni, Ru) with environment components as well as to explain physico-chemical peculiarities of stability and corrosive dissolution in the environment of proton conductive low temperature fuel cells.

DFT method and quantum-chemical programs NWChem 6.1.1 [1] in the cluster approximation with different exchange-correlation potentials were applied for the present modeling and calculations.

We proposed a new concept – energetically activity, determinate as a ratio of bond energies in binary nanocluster and that of pure platinum nanocluster for catalysis (oxygen reduction), corrosive (surface oxidation) and degradation processes (nanocluster poisoning by CO, H_2S and SO_2, including catalytic center blocking). The consideration of binary nanoclusters in all examples enhances energetically activity of the surface as compared with that of pure nanoclusters, the largest value being for PtCo and PtRu.

Quantum-chemical calculations established a consequence of energetical activity as decreased with size growth in the row $Pt_{12}Me_1$<$Pt_{32}Me_6$<$Pt_{42}Me_{13}$. Particularly, decrease of energetical activity for nanocluster surfaces of $Pt_{42}Co_{13}$ and $Pt_{42}Ru_{13}$ in comparison with similar 13-atomic nanoclusters occurs due to decrease of water adsorption heats, as well as that of common interaction of water molecules and hydroxyl ions, including alteration of adsorption sites of the hydroxyl from bridge to atop positions. It was shown that transition metals Fe, Co and Ni sufficiently influence on the properties of newly formed bonds Pt-CO (H_2S, SO_2) at the platinum surface, according to two prevailing mechanisms: by ligand (electronic) one, where Fe, Co and Ni changes electronic properties of the main catalytic metal – Pt or by collective (morphological) mechanism, when the second component of the binary nanoclusters alters the distribution of active centers on the platinum surface and allows another catalytic ways of reactions.

The results of the work should be applied for search, composition optimization and manufacting of nanosized binary catalysts on the basis of platinum in low temperature fuel cells.

1. *M. Valiev, E.J. Bylaska, N. Govind et all.* NWChem: a comprehensive and scalable open-source solution for large scale molecular simulations // Comput. Phys. Commun. – 2010 – **181.** – P. 1477-1489.