Density functional theory study of molecular oxygen interaction with the surface of stable binary nanoclusters of platinum and palladium

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Quantum-chemical calculations by means of DFT method showed peculiarities of electron density changes in the most active reaction sites for series of stable nanoclusters, such as $Pt_{37}X_{18}$ and $Pd_{37}X_{18}$ (where X – Cr, Fe, Co, Ni). Geometry structure as well as electronic characteristics for nanoclusters were calculated by means of self-consistent DFT method in generalized gradient approximation GGA with exchange correlation functional B88-LYP and the basis set double-zeta in valence approximation DZVP in frames of the program StoBe2007 [1].

We estimated details of molecular and atomic oxygen interaction with the surface of the most active binary nanoclusters $Pt_{37}Co_{18}$ and $Pd_{37}Fe_{18}$, situated over a monolayer substrate of graphite C_{82}. The main mechanism was proposed for this interaction. Chemical and electrochemical processes were distinctly divided, including molecular oxygen chemisorption, electron transition towards the chemisorbed molecule, dissociation of the surface oxygen molecular anion into its atom and singly charged ion and eventually reduction of the ion to the doubly charged specimen. The adsorption heat and activation energy of this stages were calculated on surface (111) for nanoclusters.

The sequence of the reactions possesses the lowest activation energies and the highest adsorption heats in three-folded sites. Therefore full reaction rate of oxygen reduction becomes extremely high.

It was shown that besides the nature of binary nanoclusters the structure of adsorptional and reaction sites is especially important. In particular, three fold position should be formed by 3 surface atoms of noble metals (Pt and Pd) with one atom of second component (Co and Fe) in the first sublayer. These nanoclusters would be proposed as effective materials for cathodes of modern low temperature fuel cells.

1. Hermann, K.; Pettersson, L. G. M.; Casida, M. E. et al. StoBe2007, Version 2.2; 2.2 ed., 2007.