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LETTERS TO THE EDITOR

Quantum-Chemical Study of Methane Dehydrogenation on Neutral, Cationic, and Anionic Clusters $Pt_{2–5}$ by DFT Method

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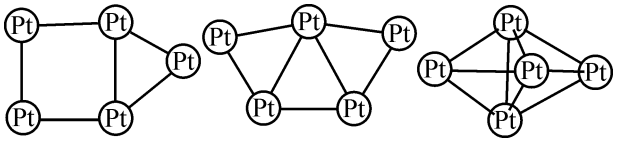
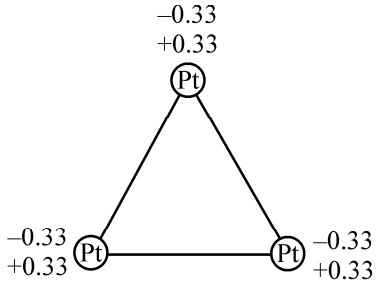
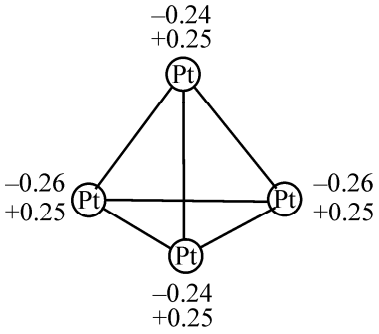
Gas phase reaction of platinum clusters with small organic molecules exhibit unusual dependence of reactivity on the size and charge of the cluster [1]. The experimental data [2, 3] indicate that the $Pt_{2–5}$ clusters have the greatest activity in the reaction of the methane activation. The studies we carried out [4] have revealed the isomers of $Pt_{2–5}$ clusters with a maximum binding energy and the corresponding multiplicity value. For the neutral $Pt_{2–5}$ clusters, the lowest energy show the triplets, except for a trigonal bipyramid [Pt_5(B)], whose multiplicity value is 5.



Pt_5(A) Pt_5(B) Pt_5(C)

The multiplicities 2 and 4 correspond to the optimal structures of the charged clusters Pt_3 and Pt_4, respectively.





The neutral triangular cluster Pt_3 is more active in the methane dehydrogenation than the neutral cluster Pt_2, and the cationic cluster Pt_3^+ is more active than the anionic cluster Pt_3^-. A higher catalytic activity of the neutral and anionic tetrahedral Pt_4 clusters as compared with the cationic Pt_4^+ cluster was revealed. For the cationic Pt_4^+ cluster, most of the transition states exceed by enthalpy the sum of enthalpies of the isolated reactants. During the reaction, a flat Pt_5 cluster is easily transferred from the structure Pt_5(A) into Pt_5(B) and back.

The rate-limiting step in the methane dehydrogenation on the neutral clusters $Pt_{2–3}$ is a process of simultaneous rupture of C–H bond due to the migration of the methylene group in the bridge position. For the rest of the studied clusters the limiting step is the elimination of the hydrogen molecule. The

process is exothermic only for the neutral and cationic cluster Pt_3, in other cases it is endothermic. While using the clusters of different size various structures are formed with a minimum relative enthalpy. The alternative mechanisms for the methane dehydrogenation that were also considered were noncompetitive due to the high activation enthalpies.

The destruction effect (lengthening of Pt–Pt bond up to cleavage) of platinum clusters on the incorporation of CH_2 group or a hydrogen atom between the platinum atoms increases as the cluster size increases. It is more pronounced in the three-dimensional structures, i.e. on the tetrahedron Pt_4 and in the trigonal bipyramid Pt_5 in particular. The maximum Pt–Pt bond length is observed as the angle Pt–Pt–H approaches 180º. Note that after the withdrawal of a hydrogen atom from the bridging position the Pt–Pt bond is always restored. In most cases the elongation of Pt–Pt bond up to rupture is characteristic of the transition states.

The data obtained allow us to explain the experimentally observed higher catalytic activity of the $Pt_{3,5}$ clusters in methane dehydrogenation with respect to the $Pt_{2,4}$ clusters, and the inactivity of the Pt_4^+ cluster.

The calculations were performed using the density-functional theory method PBE in the full electron scalar relativistic approximation in the basis of Gaussian functions L11 realized in the Priroda program [5].

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