Letters to the Editor

The DFT quantum chemical study of formation of ethane from two molecules of methane on Pt_4, Pt_6 (with and without Al_6O_9 substrate), and Pt_{14} clusters

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Experimental studies[1] showed that platinum metal clusters exhibit high catalytic activity in the dehydrogenation reaction of alkanes Processes of catalytic transformations of methane on platinum clusters are fairly complicated, therefore, to correctly interpret experimental results and purposefully select catalysts, the use of quantum chemical methods becomes important.

So far, only the process of dehydrogenation of methane on small platinum clusters has been studied,[2,3] while large clusters were studied only with respect to the adsorption of hydrocarbons.[4] The structure and reactivity of Pt_6 particles in silicalite, sodium and hydrogen forms of zeolite of the ZSM-5 type were determined.[5—8]

In the preliminary study,[9] we found the most energetically favorable pathways for the dehydrogenation reaction of methanes on neutral, anionic and cationic Pt_{2-5} clusters. The data obtained are in good agreement with the results of other theoretical and experimental works and, at the same time, significantly complement them.

The present study is devoted to the mechanism of transformation of two molecules of methane to ethane on neutral Pt_4, Pt_6 (with and without Al_6O_9 substrate), and Pt_{14} clusters, reactivity of platinum clusters differing in size and structure, as well as effect of an Al_6O_9 substrate on the formation of more complex hydrocarbons than ethane.

Calculations were performed by the PBE density functional theory method in the full-electron scalar relativistic approximation in the L11 basis of the Gaussian function realized in the PRIRODA program.[10]

Small deformation of the substrate in the adsorption process of platinum clusters and in further transformation reactions of two methane molecules was the principal criteria for the selection of the substrate. The Al_6O_9 substrate satisfies the best these criteria (Fig. 1).

Cleavage of the C—H bond in the molecule of methane on the Al_6O_9 substrate requires enthalpy of activation of 92.4 kJ mol^{-1}, with the transition state being higher in energy than the sum of enthalpies of reagents by 57.3 kJ mol^{-1}, that indicates low activity of selected Al_6O_9 substrate in the process of activation of methane.

The selected Pt_4 and Pt_6 clusters were the best in energy out of all studied by us.[11] On adsorption of Pt_4 and Pt_6 clusters on the Al_6O_9 substrate, energy of the system decreases by 242.5 and 421.7 kJ mol^{-1}, respectively, that is higher than the energies which we will further operate.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 11, pp. 2106—2108, November, 2010.
1066-5285/10/5911-2161

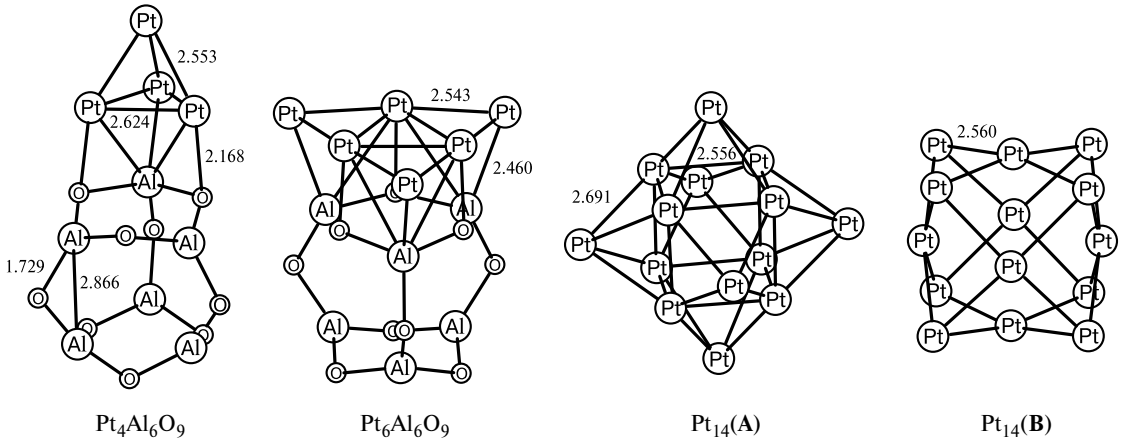

Fig. 1. Geometric parameters of optimized structures of $Pt_4Al_6O_9$, $Pt_6Al_6O_9$, Pt_{14}(**A**), and Pt_{14}(**B**); interatomic distances are shown in Å.

This demonstrate stablility of the $Pt_4Al_6O_9$ and $Pt_6Al_6O_9$ complexes formed.

We found three steps, which are rate determining in the platinum clusters differing in size and structure (Fig. 2). They are: migration of the methyl group to the bridged position between two platinum atoms (*A*); transfer of the methyl group to the platinum atom with already attached other methyl group (*B*); the process of formation of the C—C bond (*C*).*

Analysis of results obtained for the tetrahedral Pt_4 cluster with and without Al_6O_9 substrate showed that the process of formation of ethane from two molecules of methane is exothermic ($\Delta H_{298\,K}(Pt_4) = -95.8$ kJ mol^{-1}, $\Delta H_{298\,K}(Pt_4Al_6O_9) = -40.8$ kJ mol^{-1}), but it is thermodynamically favored only for Pt_4 ($\Delta G_{298\,K}(Pt_4) = -48.1$ kJ mol^{-1}, $\Delta G_{298\,K}(Pt_4Al_6O_9) = 8.2$ kJ mol^{-1}). The process *C* is a rate determining step for the Pt_4 cluster (the enthalpy of activation is 104.4 kJ mol^{-1}), while for the $Pt_4Al_6O_9$ cluster, it is the process *B* (the enthalpy of activation is 170.2 kJ mol^{-1}). In this case, the use of the substrate decreases catalytic activity of the Pt_4 cluster.

For the planar Pt_6 cluster (see Fig. 2), the substrate also decreases activity of the catalyst and enthalpy of activation of the reaction as compared to the platinum cluster without the substrate by 9.83 kJ mol^{-1}. Rate determining steps for the process with and without the substrate are different: they are, respectively, the steps *A* and *C*. In the case of Pt_6, the process is exothermic and thermodynamically favorable ($\Delta H_{298\,K} = -48.1$ kJ mol^{-1}, $\Delta G_{298\,K} = -4.8$ kJ mol^{-1}), while in the case of $Pt_6Al_6O_9$, it is endothermic and thermodynamically unfavorable ($\Delta H_{298\,K} = 23.6$ kJ mol^{-1}, $\Delta G_{298\,K} = 68.6$ kJ mol^{-1}). Therefore, for the processes studied the substrate has the same effect on the reactivity (decreases) of platinum clusters and increases relative enthalpies of the rate determining steps.

Tetrahedral Pt_4 cluster and octahedral Pt_{14} cluster (see Fig. 1, **A**) reveal activity of Pt atoms placed in the vertices and on the edges of the crystal, while planar Pt_6 and Pt_{14}

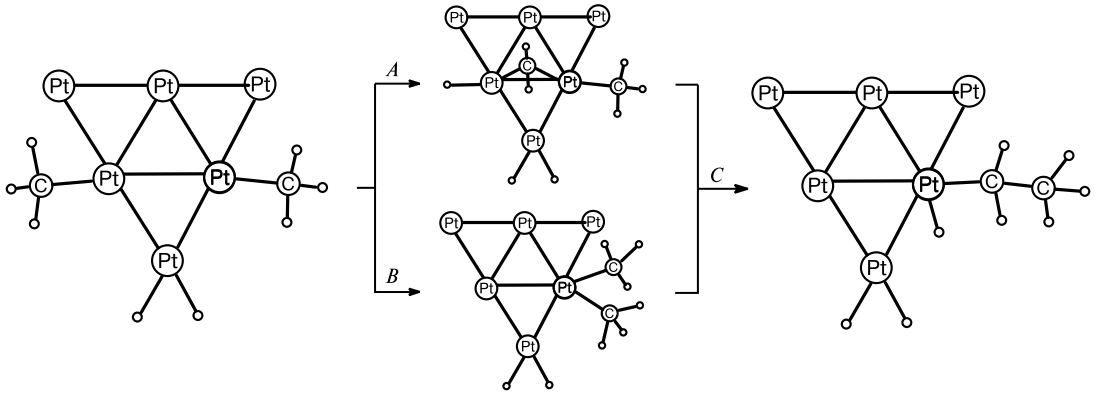

Fig. 2. Rate determining steps of the process of formation of ethane from methane using Pt_6 cluster as an example.

* Energy profiles of considered processes, as well as all the structures of intermediates and transition states corresponding to them, are available at http://www.kstu.ru/article.jsp?id=200&id_e=20615&.

clusters (see Fig. 1, **B**) (the face-centered cubic lattice) simulates the planar face of platinum. According to the calculated data, the process of obtaining ethane from methane on clusters Pt_{14}(**A**) and Pt_{14}(**B**) is exothermic ($\Delta H_{298\,K}(Pt_{14}(\mathbf{A})) = -13.5$ kJ mol^{-1}, $\Delta H_{298\,K}(Pt_{14}(\mathbf{B})) = -17.7$ kJ mol^{-1}), but thermodynamically unfavorable ($\Delta G_{298\,K}(Pt_{14}(\mathbf{A})) = 38.3$ kJ mol^{-1}, $\Delta G_{298\,K}(Pt_{14}(\mathbf{B})) = 28.4$ kJ mol^{-1}). For cluster Pt_{14}(**A**), the rate determining step is the process *A* (the enthalpy of activation is 96.4 kJ mol^{-1}), whereas for cluster Pt_{14}(**B**), the process *C* (the enthalpy of activation is 116.6 kJ mol^{-1}). Thus, it was established from the calculated data that tetrahedral and octahedral platinum clusters are more reactive than cluster simulating the planar surface. It was also shown that the reactivity of platinum decreases with the increase in the cluster size. Both these conclusions are confirmed by experimental data.[12—14]

All the calculations were performed in the Interdepartmental Super Computer Center of the Russian Academy of Sciences.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 09-03-97013-r_Povolzh´e_a).

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Received June 22, 2010;
in revised form September 2, 2010