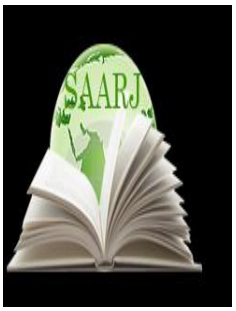

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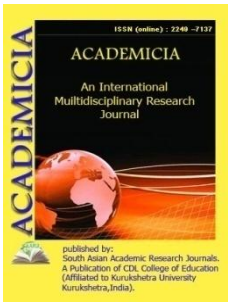

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INFLUENCE OF PLATINUM CLUSTER SIZE ON REACTIVITY IN THE PROCESS OF OBTAINING ETHANE FROM METHANE

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ABSTRACT

The paper shows the influence of platinum cluster size on reactivity in the process of obtaining ethane from methane. The enthalpy of activation and geometric parameters of intermediates and transition state for the stage of methane activation on an Al_6O_9 substrate, As well as geometric parameters of clusters used in calculations of the mechanism of ethane formation from methane have been presented. The alumina was chosen as the substrate material since experimental data indicate that it stabilizes platinum nano clusters. Our calculations confirm this. Upon the adsorption of $^3Pt_4$ and 3Pt6 clusters on the Al_6O_9 substrate, the energy of the system decreases by 242.5 and 421.7 kJ / mol, respectively, which is higher than the energies with which we will operate in the future, this is an indicator that the clusters formed on the $Pt_4Al_6O_9$ and $Pt_6Al_6O_9$ substrate are stable.

KEYWORDS: *Methane, Ethane, Platinum, Alumina, Cluster, Size, Influence, Substrate.*

INTRODUCTION

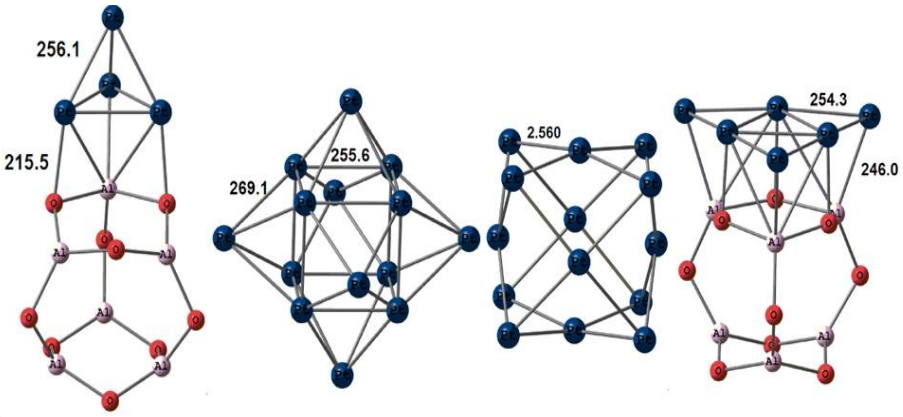
Until now, no quantum-chemical study of the theoretically and practically important mechanism of the process of obtaining ethane from methane has been carried out.

Figure 1 shows four of the six clusters in which we studied the mechanism of ethane formation from methane.

The tetrahedral cluster $^{3}Pt_4$ and the octahedral cluster $^{3}Pt_{14}$ (A) reveal the activity of platinum atoms located at the vertices and edges of the crystal, and the planar clusters $^{3}Pt_6$ and $^{1}Pt_{14}$ (B) (face-centred cubic lattice) simulate the planar face of the crystal [1-3].

MATERIALS AND METHODS

The main criteria for choosing a substrate were a small deformation of platinum clusters during adsorption onto the substrate and small deformation of the substrate itself during this adsorption and subsequent reactions. These criteria are met by the Al_6O_9 substrate (Fig. 1).



$^{3}Pt_4Al_6O_9$ $^{3}Pt_{14}$(A) $^{1}Pt_{14}$(Б) $^{3}Pt_6Al_6O_9$

Figure: 1. Geometric parameters of clusters used in calculations of the mechanism of ethane formation from methane (bond lengths in pm).

The alumina was chosen as the substrate material since experimental data indicate that it stabilizes platinum nanoclusters. Our calculations confirm this. Upon the adsorption of $^{3}Pt_4$ and 3Pt6 clusters on the Al_6O_9 substrate, the energy of the system decreases by 242.5 and 421.7 kJ / mol, respectively, which is higher than the energies with which we will operate in the future, this is an indicator that the clusters formed on the $Pt_4Al_6O_9$ and $Pt_6Al_6O_9$ substrate are stable [5-9].

Another reason the alumina support was chosen is that platinum catalysts are susceptible to sulfur poisoning. However, there are experimental data that small clusters of platinum on an alumina substrate show high catalytic activity in the presence of poisons.

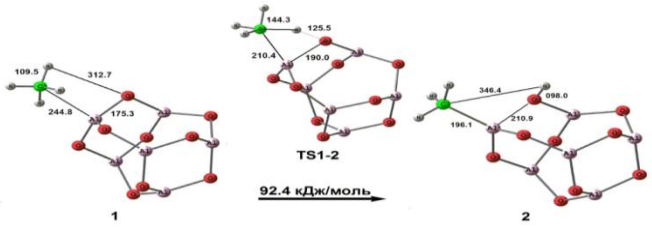


Figure: 2. Enthalpy of activation and geometric parameters of intermediates and transition state for the stage of methane activation on an Al_6O_9 substrate (multiplicity 1, bond lengths in pm).

To confirm the low activity of the selected Al_6O_9 substrate during the activation of the methane molecule, we considered the corresponding reaction (Fig. 2). To break the CH bond in the methane molecule, an activation enthalpy of 92.4 kJ/mol is required, and the TS1-2 transition state is 57.3 kJ/mol higher than the sum of the enthalpies of the reactants, while for $^3Pt_4$ TS1-2 it is 35.9 kJ/mol lower than the sum of enthalpies reagents. Therefore, this process is energetically disadvantageous.

In the process of ethane formation from methane on platinum clusters of various sizes and structures, three limiting stages were identified [10-17]. This is the migration of the methyl group to the bridging position between two platinum (I) atoms; transfer of a methyl group to a platinum atom to which another methyl group (II) is already attached; the process of formation of the C-C bond (III).

The analysis of the results obtained for the tetrahedral cluster $^3Pt_4$ with and without an Al_6O_9 substrate showed (Fig. 3) that the formation of ethane from two methane molecules is exothermic (ΔΔH298K (3Pt4) = - 95.8 kJ/mol, ΔΔH298K ($^3Pt_4Al_6O_9$) = - 40.8 kJ/mol), but thermodynamically favourable only for $^3Pt_4$ (ΔΔG298K (3Pt4) = - 48.1 kJ/mol, ΔΔG298K ($^3Pt_4Al_6O_9$) = 8.2 kJ/mol). For the $^3Pt_4$ cluster, the limiting process is the formation of the C - C (III) bond (stage 10 → 11, the activation enthalpy 104.4 kJ/mol), and for the $^3Pt_4Al_6O_9$ cluster, process (II) (stage 7 → 8, the activation enthalpy 170.2 kJ/mol). In this case, the use of support reduces the catalytic activity of the $^3Pt_4$ cluster.

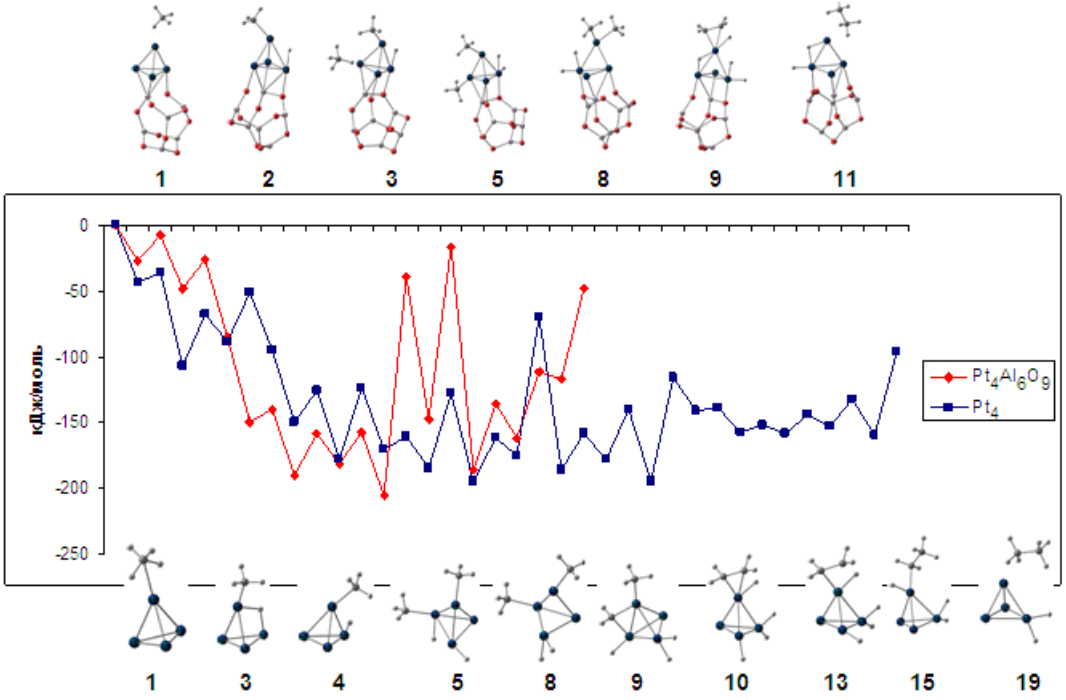


Figure: 3. Energy diagram of the reaction of ethane formation from methane on a 3Pt4 cluster with and without an Al_6O_9 substrate. The sum of the formation enthalpies of isolated reagents is taken as zero.

As an alternative mechanism, using the example of the 3Pt4 cluster, we considered the process of ethylene formation (Fig. 4). Initially, the formation of ethylene is more energetically favorable than the formation of ethane [18-23]. Thus, when a hydrogen atom migrates from a carbon atom to a platinum atom, the enthalpy of the system decreases with the formation of structure 14a with the lowest relative enthalpy (-243.6 kJ/mol). However, the process of detachment of a carbon atom from a platinum atom (stage 14a → 15a) occurs with a barrier of 114.2 kJ/mol, which is higher than the barrier of the limiting stage of the formation of a carbon-carbon bond (stage 10 → 11, activation enthalpy 104.4 kJ/mol).

The process of further carbonization of platinum is energetically unfavourable, which is confirmed by structure 19a, the relative enthalpy of which is 170 kJ/mol higher than the sum of the enthalpies of the reactants [21-26]

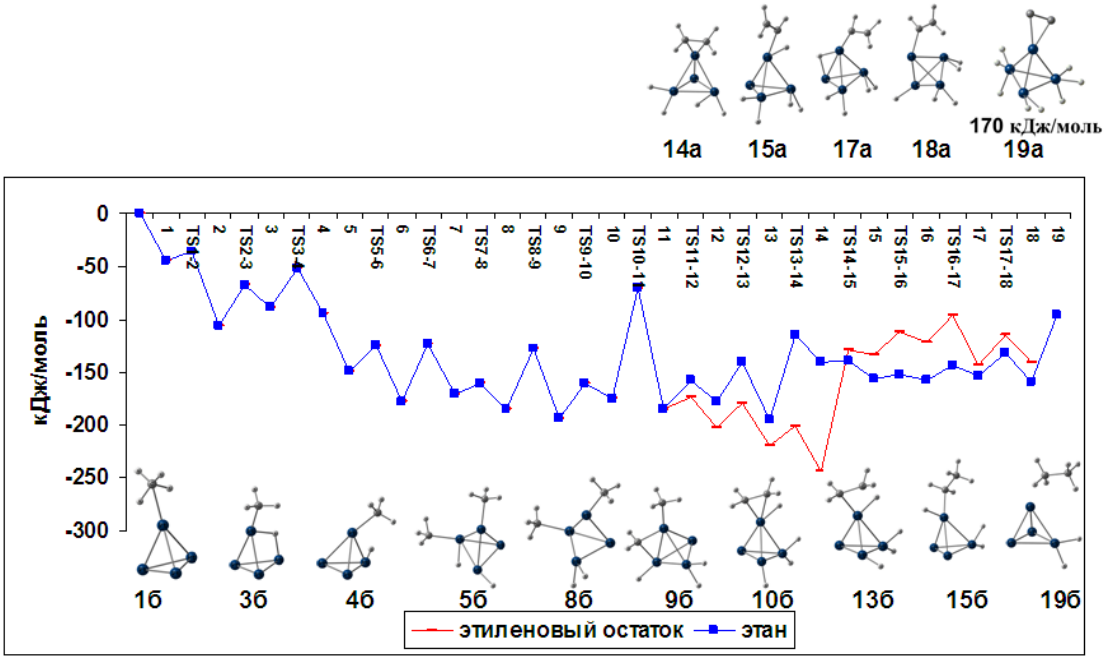


Figure: 4. Energy diagram of the reaction of ethane and ethylene formation from methane on the $^{3}Pt_4$ cluster. The sum of the formation enthalpies of isolated reagents is taken as zero.

RESULT AND DISCUSSION

The analysis of the results obtained in the study of the conversion of methane to ethane on platinum clusters of various sizes deposited on a substrate (and without it) made it possible to reveal some important regularity in the course of this process. It was found, that the values of the activation barriers for the main stages with respect to the sum of the enthalpies of isolated reagents for $^{3}Pt_4$, $^{3}Pt_{14}$ (A) and $^{3}Pt_6$, $^{1}Pt_{14}$ (B), respectively, are quite close.

It follows from this that the results for small clusters can be used, to simulate methane conversion processes on clusters of much larger size.

Thus, the order of relative stability for neutral, cationic, and anionic platinum clusters has been determined. The most stable isomers of neutral Ptn clusters up to n = 6 have a planar structure. It

is shown that the adsorption of a hydrogen molecule on small platinum clusters occurs without activation. The resulting $Pt_{4-9}H_2$ hydrides are elongated to 306.3 pm. Pt-Pt bonds and a different order of relative stability than the initial Pt_{4-9} clusters. For Pt4H2, the tetrahedral arrangement of platinum atoms becomes the most favorable. The limiting stages of the methane dehydrogenation reaction on neutral, cationic and anionic platinum clusters have been identified.

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