

THE METHANOL MOLECULE INTERACTION WITH OXYGEN FUNCTIONAL GROUPS ON GRAPHENE-LIKE MATERIALS: A QUANTUM CHEMICAL STUDY

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Methanol conversion into dimethyl ether (DME) is a large-scale industrial process. Therefore, huge attention is focused on finding ways to reduce the cost of the relevant process. Developing a novel carbon catalyst for the synthesis of DME is one of the main routes to increasing the effectiveness of methanol utilization. There are presented experimental works where carbon materials, particularly, carbon nanotubes [1], activated carbon, and graphene materials, are used as catalysts. However, the reaction mechanisms of methanol conversion interaction on carbon materials are still under discussion.

This report presents the results of quantum chemical calculations (DFT, B3LYP/6-31G**) of the main elementary stages of methanol dehydration to DME on graphene-like materials (GLM). As a model of GLM was used the polycyclic aromatic hydrocarbon (PAH) C₉₆H₂₄ (hydrogenated graphene) and its derivatives – PAH functionalized by oxygen functional groups like hydroxyl (–OH) and carboxyl (–COOH). To account for the dispersing contribution to the energy of intermolecular complexes formation, the dispersion correction by Grimme was used too. The structure optimization of derivatives was carried out with different multiplicities (M), and the ground electronic state (GES) of the clusters was found. The initial step of interaction is physical adsorption (see figure). In the first step, the methanol molecule is adsorbed on a functional group with a negative energetic effect. The second step of interaction is dissociative adsorption of the methanol molecule: the oxygen-hydrogen bond of methanol was broken, and the molecule of water was formed. The role of the water molecule in the reaction of methanol dehydration into DME was studied. Two cases of further reaction steps were considered: the addition second methanol molecule when the water molecule was present at the intermediate stage and the desorption of the water molecule from the reaction mixture before the second methanol molecule was added. Computed reaction profiles of the reactions were investigated.

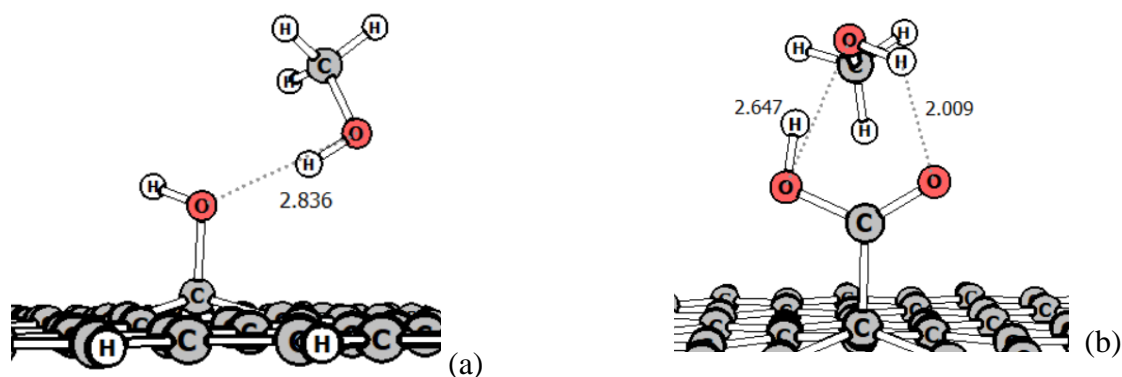


Fig. Physical adsorption of methanol molecule on GLM functionalized by hydroxyl (a) and carboxyl (b) group. The distance between atoms in Å.

Obtained results show that active sites in dehydration reactions are hydroxyl and carboxyl groups. The presence of a water molecule provides higher binding energy for the second methanol molecule in the reaction of methanol dehydration to DME.

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1. Yan P., Zhang X., Herold F., Li F., Dai X., Cao T., Etzold B. J. M., Qi W. Methanol oxidative dehydrogenation and dehydration on carbon nanotubes: active sites and basic reaction kinetics // *Catal Sci Technol.* – 2020. – 10, N 15. – P. 4952–4959.