Ab Initio Free Energy Profiles of Methane Decomposition on Graphene

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The aim of this study is to determine the shape of free energy profiles and, in particular, energy barriers of methane decomposition on graphene. This is one of chemically complex processes occurring in chemical vapor deposition (CVD) growth of graphene from hydrocarbon precursors. The reaction occurs in steps that can be written out with the chemical equation $CH_n \rightarrow CH_{n-1} + H$. This issue has been previously studied on (111) nickel surface [1].

Ab initio molecular dynamics is employed to simulate the reactions. It is based on density functional theory and allows us to determine accurate quantum-mechanical forces acting on atoms. Simulations are done in temperature controlled ensemble. The temperature is either close to the standard state (300 K) or at typical CVD growth temperature (1200 K). Holonomic constraints are imposed over selected ionic degrees of freedom – bond lengths or angles. They determine reaction coordinates (RC) of decomposition or adsorption (Fig. 1). Free energy profiles are calculated by integrating the constraint force at varying RC [2].

Calculated energy barriers on graphene (1.68, 2.04, 2.03, 1.37 eV) are significantly lower than experimental bond dissociation energies for isolated molecular gases (4.55, 4.79, 4.39, 3.51 eV) [3]. This shows that graphene acts as a catalyst for methane decomposition.

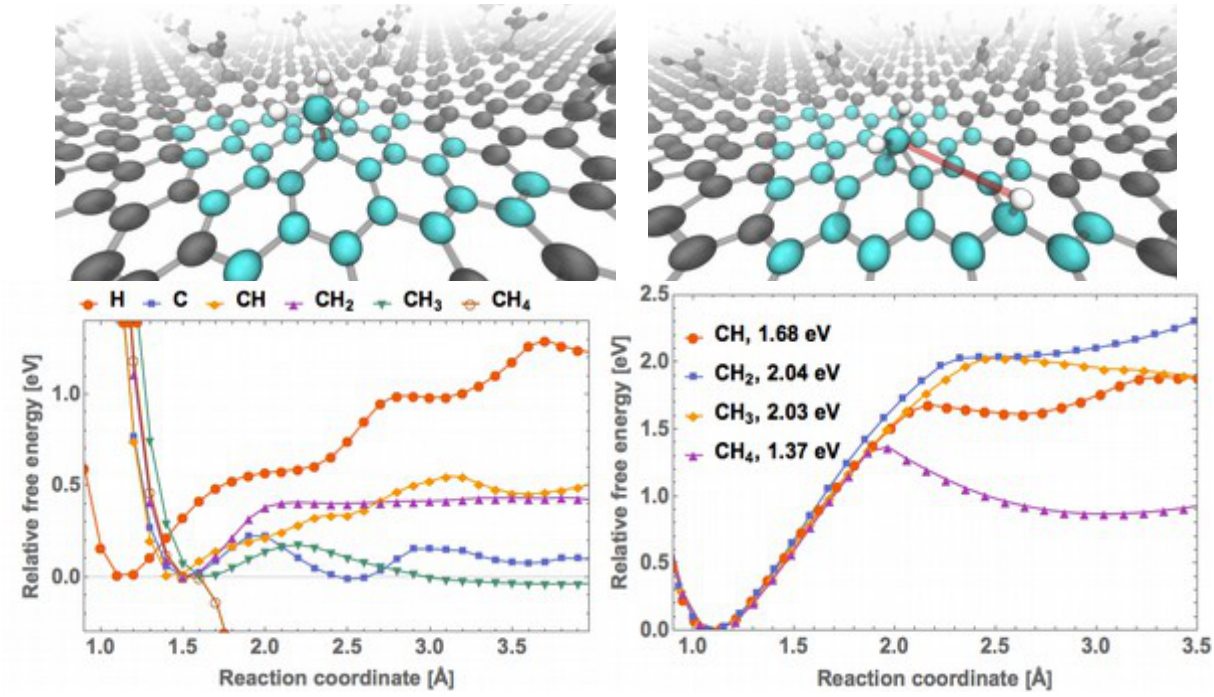

Fig. 1: Molecular schemes of CH_3 adsorption and decomposition (top panels, RCs highlited in red) and corresponding energy profiles for all steps (bottom panels). Bottom right panel legend lists reaction barriers.

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[2] T. Mulders *et al.*, *J. Chem. Phys* **104**, 4869 (1996)
[3] S.J. Blanksby, G.B. Ellison, *Acc. Chem. Res.* **36**, 255 (2003)

Acknowledgements:
The research has been performed in the framework of the ShaleSeq project (Physicochemical effects of CO2 sequestration in the Pomeranian gas bearing shales) funded from Norway Grants in the Polish-Norwegian Research Programme operated by the National Centre for Research and Development, grant no. POL-NOR/234198/100/2014.