

DFT mechanistic studies on CH₄ coupling over Au-TiO₂ catalysts

Dorota Rutkowska-Zbik,* Vidya Kaipanchery, Renata Tokarz-Sobieraj

Jerzy Haber Institute of Catalysis and Surface Chemistry Polish Academy of Sciences, ul. Niezapominajek 8, 30-239 Krakow, Poland

dorota.rutkowska-zbik@ikifp.edu.pl

Direct conversion of methane into fuels and platform molecules has been for a long time a “holy grail” in chemistry. The high C-H bond energy (434 kJ mol⁻¹), absence of functional groups and polarity result in a very low methane chemical reactivity. High temperatures and high pressures are generally required to accelerate methane chemical transformations and operation at practical rates. These harsh conditions, however, lead to huge energy consumption, often-important emission of CO₂, parasitic formation of by-products and fast catalyst deactivation. Light is an ideal alternative energy source and is largely used in combination with semiconductors to drive chemical reactions. Photocatalysis has been also considered as one of pathways to break the thermodynamic barrier. Experimental studies show that Au-TiO₂ catalyst under UV/VIS light irradiation is selective in the oxidative coupling of methane to ethane.

To understand the observed reactivity, we performed quantum-chemical calculations in the frame of Density Functional Theory (DFT) and Time-Dependent DFT (TD-DFT) with a B3LYP+D3 functional and the def2-TZVP basis set. The geometry and electronic structure of the catalytic system was characterized by computing selected bond lengths, Mayer bond indices, ESP charges on the exposed surface sites, and the DOS plots. Then, methane interaction with Au_n/TiO₂ (and the isolated Au_n and TiO₂ fragments) was considered to find the most probable active site for the reaction.

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