

# DFT Studies on Metal-Heteropolyacid-titania Systems for Methane Coupling and H<sub>2</sub> Generation

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Low-temperature valorisation of CH<sub>4</sub> is a holy grail for chemists because its C-H bonds are the most difficult to break and functionalise. In recent years a considerable effort is undertaken to transform methane into more reactive and useful chemicals. Methane coupling into higher hydrocarbons is one of such processes. In typical conditions (e.g. when catalysed by Mo-ZSM-5), the process requires high temperatures (above 750°C). The conditions can be much more benign if the reaction is carried under photochemical conditions. Recently, the metal (silver, palladium) - heteropolyacid - titania hybrid materials were proposed as photocatalysts for methane coupling [1]. The aim of our contribution is to explore the reactivity of these systems for CH<sub>4</sub> activation and C-C bond formation by performing theoretical calculations.

As models of the catalysts, the M<sub>13</sub>-(TiO<sub>2</sub>)<sub>34</sub>, HPA-(TiO<sub>2</sub>)<sub>34</sub>, and M-HPA (where M = Ag, Pd; HPA = heteropoly tungstate, heteropoly molybdate of Kegging structure) systems were proposed. The quantum chemical calculations were performed within Density Functional Theory (DFT) and Time-dependent Density Functional Theory (TD-DFT) with def2-SVP basis sets, PBE functional with +D3 Grimme's correction using the Turbomole program.

We considered the possibility to activate methane at the surface of the catalysts and, for comparison, in the gas phase by reactive oxygen species (ROS) which can be formed under photocatalytic conditions from O<sub>2</sub> and H<sub>2</sub>O at the TiO<sub>2</sub> surface (O<sub>2</sub><sup>·-</sup>, OOH<sup>·</sup>, OH<sup>·</sup>). The comparison of the computed energy barriers needed to split the first C-H bond varies depending on the system. It amounts to 39.9 kcal/mol for TiO<sub>2</sub><sup>+</sup> (modelling photo-excited titania), but when ROS are formed in the reaction mixture, they can also activate methane with much lower energy input (e.g., 15.4 kcal/mol in case of the reaction with OH<sup>·</sup>), in agreement with EPR experiments under *in-situ* conditions. Then, the mechanism of the C-C bond coupling on different catalysts was modelled. Additionally, the activity of the studied materials was tested for photocatalytic H<sub>2</sub> generation, as a side-product of methane coupling.

[1] Y. Wang, C. Dong, D. Hu, R. Tokarz-Sobieraj, D. Rutkowska-Zbik, K. Ben Tayeb, A. Addad, V. Butenko, E. de la Torre Miranda, M.N. Tran, P. Simon, O. Safonova, V. Briois, V. V. Odomsky, A.Y. Khodakov, Appl. Catal. B Environ. Energy. 358 (2024) 124400.