

Computational Investigation of the Conversion of Methane to Products

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The optimal use of methane (CH₄) from natural gas has been shown as a greener and more economical feasible mid-term alternative for this long-period transition, i.e., from non-renewable to renewable energies.[1] However, its complete efficiency as an energetic matrix relies on its conversion into other high-value chemicals, such as methanol (CH₃OH), formic acid (HCOOH), carbon monoxide (CO), etc. However, regardless of the methods nature, i.e., direct or indirect (via syngas), CH₄ conversion is highly dependent on C–H activation and further dissociation, which is commonly facilitated through the use of distinct catalysts classes, e.g., metallic substrates, oxides, zeolites, etc.[1] Therefore, in this present work, we aim to provide an overview of our efforts through the use of DFT, regarding CH₄ activation and conversion processes using different types of catalysts substrates. Therefore, we showed that the d-states occupation on 3*d*-TM₁₃ clusters (TM = Fe, Co, Ni, and Cu) affects strongly medium-strong chemisorbed systems, i.e., CO/TM₁₃ and H₂/TM₁₃, while for weak physisorbed systems, i.e., CH₄/TM₁₃ and CH₃OH/TM₁₃, the d-states occupation is not crucial, as local polarization takes place (electrostatic effects).[2] Thus, more recently, we elucidate the importance to include van der Waals' effects on those

types of interactions.[3] In other work, our results showed that the quantum size effects play only a crucial role at small TM_n clusters regimes $n < 7$ in modulating the adsorption energy, and hence, also the activation energy magnitude of CH_4 activation processes towards CH_3+H formation.[4] Finally, we elucidated that the activation and dissociation of CH_4 into $CH_n+(4-n)H$ systems, i.e., dehydrogenated species, on 3d- TM_{13} clusters can be rationalized into a concerted interaction mechanism, where charge transfer, *sp-d* coupling, and unpaired electrons take place, explaining the increase of adsorption energy magnitude along the dehydrogenation process. Furthermore, there is a thermodynamic preference to form carbon depositions on the Ni_{13} cluster as the CH_4 dehydrogenation is facilitated energetically, both kinetically and thermodynamically, on that substrate.[5] Conversely, Peraça et al.,[6] showed that the formation of CO is energetically preferred for CH_4 dehydrogenation on the $(CeO_2)_{10}$ cluster, indicating the preference for *syngas* formation rather than CH_3OH ; however, methanol can be further indirectly obtained.

Keywords: DFT, methane, clusters, *syngas*, methanol

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