

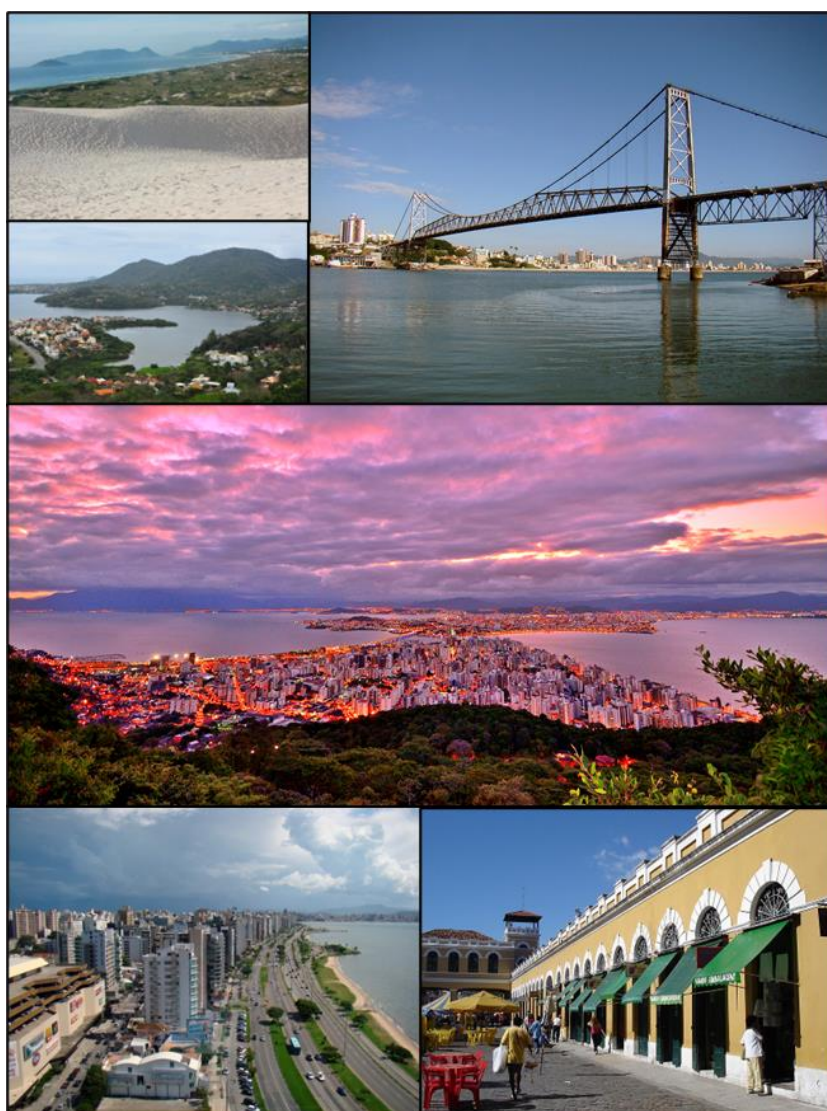


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ABSTRACT BOOK



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Exploring Methane Activation and Conversion via Computational Chemistry and Data Science Approaches

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The use of methane (CH₄) from natural gas is a greener and economically viable option for transitioning to renewable energy. Its optimal use depends on converting CH₄ into high-value chemicals like methanol (CH₃OH), which requires C–H bond activation typically facilitated by catalysts such as metals, oxides, and zeolites. This work presents an overview of our DFT studies combined with data mining techniques on CH₄ activation and conversion. Our initial study [1] showed that CH₄ *activation and dehydrogenation on 3d-TM₁₃ clusters* (TM = Fe, Co, Ni, Cu) involves a concerted interaction mechanism, driven by charge transfer and *sp-d* coupling, resulting in systematically increased adsorption energies during dehydrogenation. Felício-Sousa et al. [2] found that the *d*-states occupation of the TM atoms, plays a crucial role in chemisorbed systems (e.g., CO/TM₁₃, H₂/TM₁₃) but has a weaker effect on physisorbed ones like CH₄/TM₁₃. Further studies [3] highlighted that quantum size effects (QSE) are significant for small for TM_{*n*} clusters (*n* < 7), affecting adsorption and activation energies, with Ni_{*n*} clusters (*n* = 10-14) showing thermodynamic and kinetic favorability. Peraça et al. [4] observed that CH₄ dehydrogenation on (CeO₂)₁₀ clusters favors CO formation, suggesting syngas production over CH₃OH. More recently, we studied CH₄ activation on TM/CeO₂(111) systems (TM = Fe, Co, Ni, Cu, Zn, Ru, Rh, Pd, Ag, Ir, Pt, Au), finding that stable TM adatoms reduce Ce⁴⁺ to Ce³⁺, enhancing methane dehydrogenation as the TM period increases, while C–H activation barriers generally decrease with increased CH₃ *adsorption energies*. [5] Finally, our investigation into the whole mechanism of partial oxidation of CH₄ on 3d-TM₁₃ clusters, showed that on Ni₁₃, CH₃OH is preferred formed via the hydroxyalkyl pathway over the alkoxy pathway, making CO less favorable as a complete oxidation product.[6]

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