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A DFT Investigation of CH_4 Activation and Dehydrogenation on Ceria Clusters

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Highlights

Methane has a high propensity to be converted into syngas and other important compounds for the production of energy inputs.

Resumo/Abstract

Methane is a greenhouse gas that has a high potential to trap radiation in the atmosphere. It also a major constituent of natural gas and offers the possibility of being converted into other chemicals, making it a valuable resource for the production of energy during the transition from non-renewable to renewable sources. Due to the high stability of this molecule, one of the great problems of this process relates to the CH_4 activation, which allows the first C-H bond break. In recent decades, finding catalytic materials that can transform methane into high-value chemicals like CH_3OH and H_2 has been suggested as a potential solution. In this sense Ceria based materials can be a great catalyst candidate since the interaction between the H atom from molecule and O^- centered from the cerium oxide can lead to the activation of methane and the subsequent dehydrogenation. Then, in this work we report a computational investigation about the CH_4 activation and dehydrogenation considering $(CeO_2)_{10}$ cluster as a catalyst. Our calculations are based on Density Functional Theory (DFT), employing the Perdew-Burke-Ernzerhof (PBE) formalism, combined with the Unity Bond Index-Quadratic Exponential Potential approach (UBI-QEP). To improved the correct description of the coulomb interaction for localized *f*-states from Ce atoms and the long-range interactions, we employed the Hubard term (U) and the van der Waals corrections (D3), respectively. Our results showed that the adsorption of this species generates a polaron leading the presence of Ce^{3+} and a consequent geometric distortions which affects the reactivity of the material. In this sense, the H co-adsorption site can influence the energetic barrier value of the first C-H bond break that varies from 0.54 eV to 0.81 eV and are considered a destabilizing factor, once compete for the same adsorption site of the molecule. As the dehydrogenation becomes, a strong tendency towards complete dehydrogenation was observed leading to the formation of other compounds, e.g. CH_3OH and syngas, two essential chemicals for the generation of energy inputs.

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