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Breaking Simple Scaling Relations Through Metal-Oxide Interactions: Activation of Methane on M-CeO₂ (M= Pt, Ni or Co) Interfaces

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Methane (CH₄) -a greenhouse gas (GHG)- is difficult to convert to upgraded fuels or chemicals because of the high C-H bond strength in the molecule and its non-polar nature. Enabling low-temperature activation of CH₄ is a major technological objective. Descriptors and scaling relations for the first dehydrogenation of CH₄ provide guidelines for comparing and predicting the performance of potential new catalysts [1]. In this work, we investigate how to use metalsupport interactions to enhance chemical reactivity for methane activation, breaking existing scaling relations [1]. In this talk, results obtained using computational models of Pt/ceria systems will be discussed, which are consistent with those of experimental model [2] as well as powder [3] catalysts, and thus help to bridge the materials gap between them. The experimental AP-XPS data indicates that methane dissociates on the Pt/CeO₂(111) surface and a Pt/CeO₂ powder at temperatures between 25 and 427 °C. When compared to other low-loaded M/CeO₂(111) (M = Cu, Ni or Co) systems [4,5], Pt nanoparticles supported on ceria produce the largest amount of CH_x, and is the most active for the conversion of carbon dioxide and methane. The theoretical results for a number of low-loaded metal/ceria systems show that the proposed linear scaling relation,[1] does not generally hold for ceria-supported metal nanoparticles, for which smaller C-H bond activation energy barriers than predicted are found, by up to ~1 eV. Strong interactions between the small metal particles in direct contact with the ceria support lead to the stabilization of both the CH₄ molecule and the CH₃+H dissociation product, producing active and stable catalysts for methane activation. Our findings should be useful in the rational design of catalysts for reactions involving C-H bond dissociation [2].

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