Engineering the reactivity of metal catalysts: a model study of methane dehydrogenation on Rh(111)

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Tuning the relative reaction rates of the different steps of methane dehydrogenation would allow to optimally design important chemical processes such as, e.g., the production of hydrogen from methane or the conversion of the latter to methanol or to ethane. The efficiency of transition-metal catalysts to promote these and other related reactions is limited by the tendency of dehydrogenation to proceed until graphite is eventually formed on the surface, thus poisoning the catalyst.

In this work we have investigated the dependence of the reaction rates of the first two steps of methane dehydrogenation on the structure and local chemical composition of the metal catalyst substrate, in the specific case of Rh(111), using density functional theory and the nudged elastic band method to characterize the reaction path. We have found that, although the barrier for the dehydrogenation of methane ($CH_4 \rightarrow CH_3 + H$) decreases as expected with the coordination of the binding site, the dehydrogenation of methyl ($CH_3 \rightarrow CH_2 + H$) is hindered at an ad-atom defect, where the first reaction is instead most favored. Preliminary results will also be reported on the role of the local chemical composition (including hetero ad-atom defects and surface alloying) on the various reaction barriers.