Hydrogen adsorption on and spillover from Au- and Cu-supported Pt-3 and Pd-3 clusters: a density functional study

Motivated by the use of electrodes modified at the nanoscale by supported metal species, we studied computationally how the reactivity changes in such a composite system compared to the reactivity of the individual systems, metal clusters and metal surfaces. Specifically, we examined hydrogen adsorption on and hydrogen spillover from Au- and Cu-supported Pt-3 and Pd-3 clusters, using a method based on Density Functional Theory. Two distinctive types of sites were found for the adsorption of atomic hydrogen: (i) on the supported clusters and (ii) at the cluster-substrate interfaces. The adsorption energy of hydrogen on the supported clusters is similar to 20 kJ mol\(^{-1}\) smaller when the cluster is supported by Cu instead of Au. In contrast, the substrate has no effect on hydrogen adsorbed at the cluster-substrate interfaces. Adsorbed Pt-3 and Pd-3 clusters locally modify the reactivity of the substrates as quantified by the reduced adsorption energy of hydrogen compared to the corresponding clean substrate. Hydrogen dissociative adsorption followed by spillover is thermodynamically and kinetically favored for clusters supported on a Cu surface, but not on Au. Moreover, spillover of hydrogen is more likely from metal-supported Pd than Pt clusters as revealed by barriers that are calculated 40-50 kJ mol\(^{-1}\) lower in energy.
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