

Performance of Density Functionals in Modeling the Decomposition of CH₃OH by Cu₄ Cluster

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Heterogeneous catalysts are a critical part of industrial chemistry, primarily as a tool for more economically and ecologically efficient chemical processes. The activation of small abundant organic molecules such as methanol, catalyzed by metals, leads to hydrogen gas with a high atomic economy, which gives to the reaction the potential role in the development of such a promising source of energy. It is thus desirable to develop theoretical methods that can predict trends in catalytic activity and predict active catalyst for industrially important reactions. We are interested in the efficacy of DFT for modeling heterogeneous catalysis; this has to be ascertained through benchmark studies. In this study, the mechanism of the dissociation of CH₃OH by Cu₄ clusters is computed with DFT and with CCSD(T)/CBS-extrapolated. Adsorption energies of all possible decomposition products, reaction barriers for the cleavage of all possible bonds, and the reaction energies of those cleavages have been computed. We have undertaken a benchmarking study of various methods on the decomposition of methanol on small copper clusters with a wide range of DFT methods. The simulation of the reactivity of such small metal clusters is interesting both for elucidating the participation of the small clusters and also as model for the molecular-metal interactions in nanoparticles and surfaces.

