

Abstract

One of the most pressing dilemmas of contemporary chemical research is how to efficiently and economically convert small and inert molecules, such as the vastly abundant H_2 , CH_4 , CO_2 and H_2O , into primary energy carriers and industrially valuable compounds; this field is called “small molecule activation”. Strongly related to this problem is the development of artificial photosynthesis that converts solar into chemical energy, which is the most promising approach for securing an inexhaustible, environment-friendly solution for sustainable energy conversion. Critical in this research is the development of new, robust, clean and efficient catalysts, which are capable of facilitating the activation of inert small molecules and promoting the most critical steps of their various catalytic transformations.

In this thesis we use computer aided modeling techniques, based on first principles quantum chemical methods, to gain insight into important aspects of the working mechanisms of three different types compounds occurring in homogeneous and heterogeneous catalysis. In homogeneous catalysis, we focus on a detailed scrutiny of the redox non-innocent behavior of ligands in transition metal complexes and bulky substituents triggered frustration of Lewis acid-base pairs. Additionally, metal substituted zeolites, typical heterogeneous catalysts, are investigated. In these studies, the electronic and structural aspects and their consequences for selected homogenous and heterogeneous catalytic reactivity were investigated within the framework of conceptual and computational Density Functional Theory (DFT). The conceptual understandings of these phenomena coupled to a systematic design strategy would allow, on the long run, the rational design of the catalytic activity of the corresponding systems exhibiting desired and well-engineered properties and reactivity. We also introduce our in-house developed computation-manager program, DOMINO, which was designed to facilitate the large-scale computational work involved in the research.