Abstract

Density Functional Theory of Free and Oxide Supported Metal Nanoclusters and Nanoalloys: A Heterogeneous Catalysis

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Heterogeneous catalysis, a subject of utmost importance in present days, is attributed to its great potential in the modern production of chemical products, and also in other fields such as pollution and environment control. The free and oxide-supported metal nanoclusters and nanoalloys are particularly interesting in the context of heterogeneous catalysis. Nanoclusters made up of transition metals of group 10 (Ni, Pd, Pt), group 11 (Cu, Ag, and Au) and alloying between these two groups offer excellent physical, catalytic (improved activity, selectivity, and stability enhancement), optical, electronic and magnetic properties with the possibility of tuning the size, dimensionality, charging state of supported metal clusters, and/or the thickness, morphology, chemical composition of the underlying substrate. At the same time, metal oxides possess unique structural and electronic properties that render them promising candidates in heterogeneous catalysis. In this thesis, a good balance between accuracy and computational cost in describing electronic structure was sought via the spin-polarized density functional theory (DFT) method and the climbing image nudged elastic band method (CI-NEB) was used to probe the activation energies, reaction energies, transition state structures, and charge analysis results are used to explain the underlying mechanistic pathways. Chapter 3, comprises the concept of alloying effect on the elimination of carbon monoxide (CO) poisoning over Cu doped Ni_nCu clusters during CO oxidation with the systematic computational calculations. Chapter 4 provides mechanistic insights on the fundamental properties of icosahedral Pd_mCu_n Clusters (m + n = 13). Hydrogenation of carbon dioxide (CO_2) is a complex process with many potentially valuable products including methane, methanol, and higher hydrocarbons and alcohols. Chapter 4 also examines the CO_2 hydrogenation over the most stable Pd_5Cu_8 cluster for the production of methanol, formic acid, and methane. Chapter 5 presents the role of $Cu_2O(111)$ supported Pt_4 and Pt_3X (where X = Co and Au) nanoclusters in CO oxidation reaction. This thesis defines a novel strategy to design new catalysts and introduce novel and practical methodologies to control their catalytic performance at the atomic scale.